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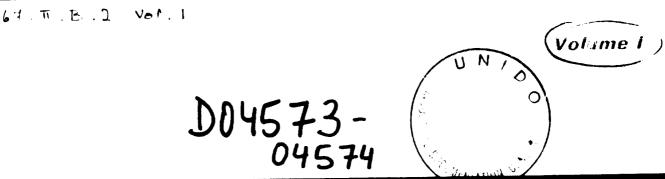
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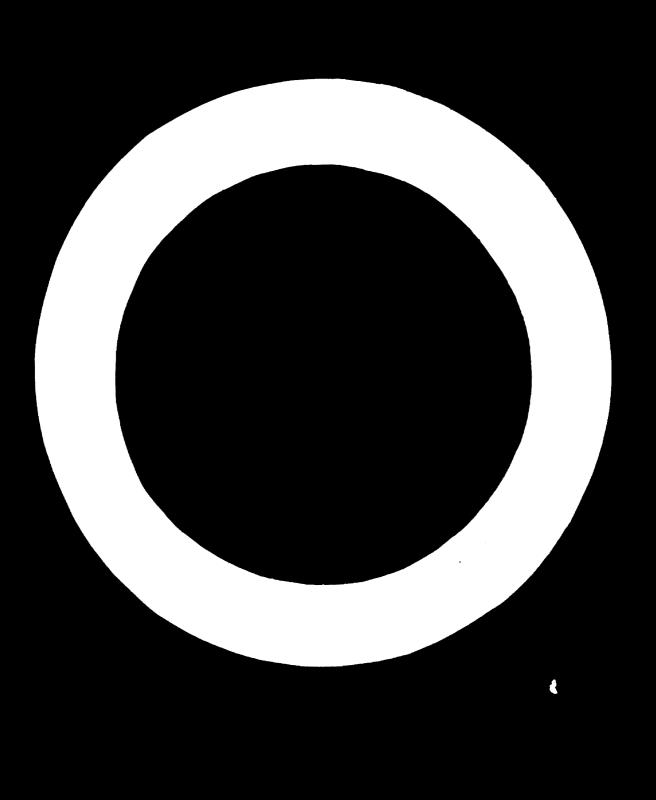
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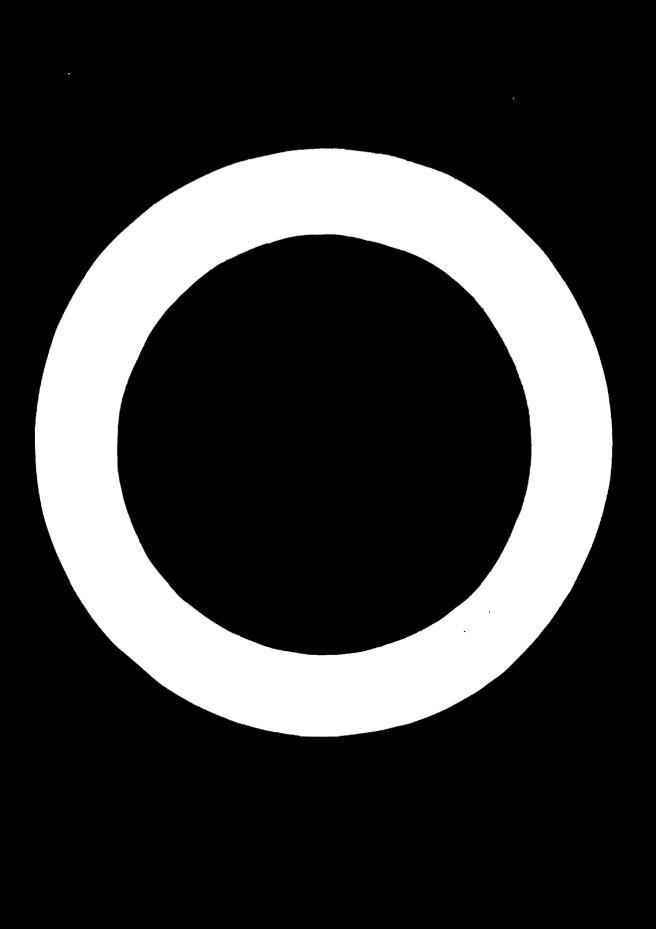
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## STUDIES IN PETROCHEMICALS







Volume I

# STUDIES IN PETROCHEMICALS

**Presented at the United Nations** Interregional Conference on the Development of Petrochemical Industries In Developing Countries

Teheran, Iran 16-30 November 1964



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### PREFACE

The first United Nations Interregional Conference on the Development of Petrochemical Industries in Developing Countries was held in Teheran, Iran, from 16 to 30 November 1964. The final report of the Conference has been issued as a separate publication (ST/TAC/Ser.C/83).<sup>1</sup>

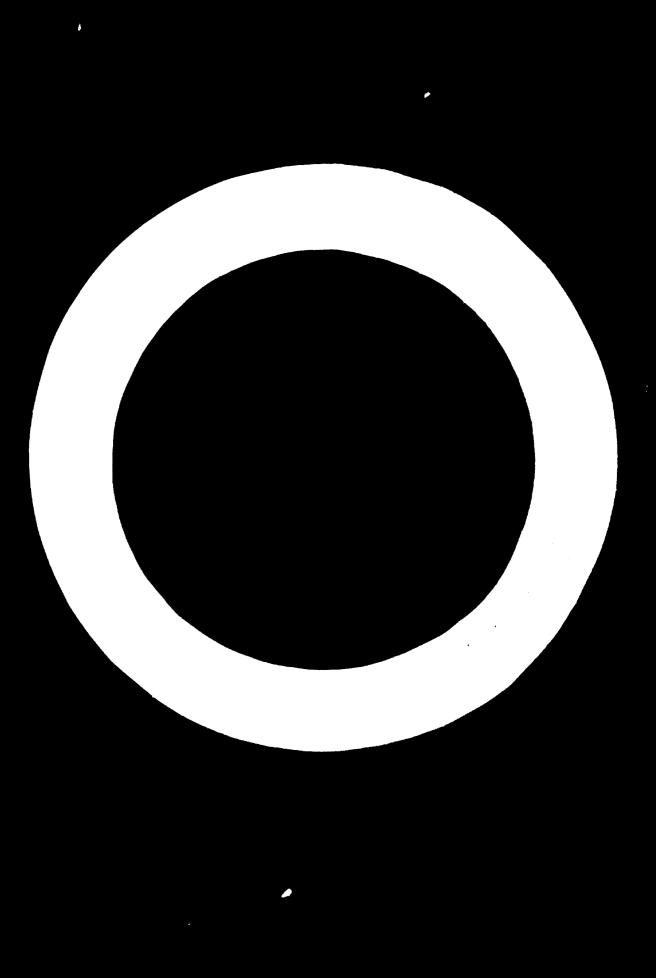
The present volumes contain studies on petrochemicals submitted to the Conference. The material is arranged according to subject and conforms to the agenda of the Conference. Each chapter begins with a short introductory summary of the subjectmatter.

In general, the studies and reports are printed in the form in which they were submitted. However, corrections have been incorporated, some of the figures have been rearranged and some minor editorial changes have been made. The usage and style of the original texts have usually been retained. Bibliographical and other references have, wherever possible, been verified. Some of the bibliographical lists have been omitted and some references have been printed as foot-notes.

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<sup>1</sup> United Nations publication, Sales No. : 66. II.B. 14.



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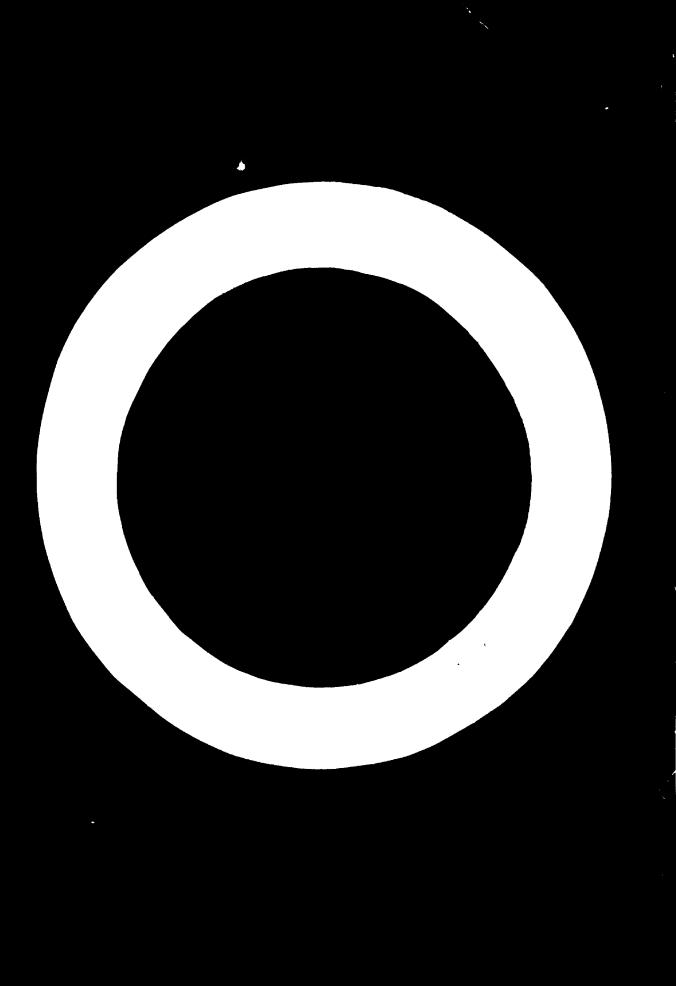
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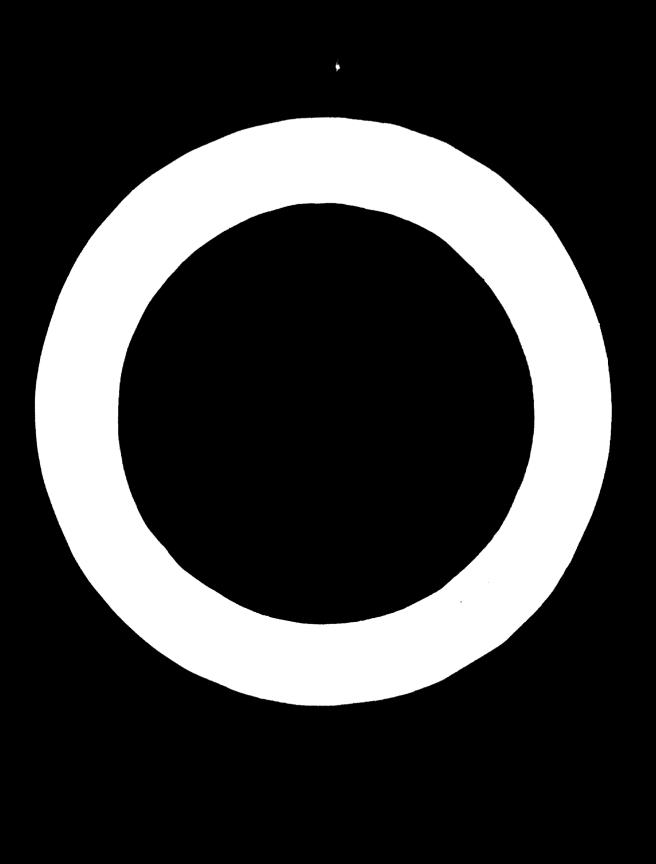
Chapter I

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## CHARACTERISTICS OF THE PETROCHEMICAL INDUSTRY AND PROSPECTS FOR ITS DEVELOPMENT

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### INTRODUCTORY SUMMARY

The papers in this chapter, taken together, discuss not only the general characteristics of the petrochemical industry in industrialized countries, but also the major considerations underlying its establishment and development in the developing countries.

The importance of this latter topic stems from the fact that developing countries, especially those with abundant petroleum and natural gas resources, have shown increasing interest in the development of petrochemical industries. The petroleum refineries which are being established in a number of countries also provide a basis for establishing petrochemical complexes. In addition, there are countries with an already existing organic-chemical industry, which are substituting oil and gas for other traditional inputs, such as raw materials derived from coal or vegetables.

This industry is considered to be of strategic importance in inducing further industrial development because most of its output goes to other producing sectors. It shares this characteristic of intermediate manufacture with other industries such as iron and steel, paper and its products, and petroleum products.

The following characteristics of the petrochemical industry to be considered in establishing a programme for its development were stressed:

(a) A high degree of product homogeneity and standardization continuity and stability of operations;

(b) A high capital intensity;

Survey and a second

(c) A high proportion of skilled labour including scientists and technicians;

(d) The availability of alternative production processes and raw materials and a high rate of technological change.

## 1. GENERAL CHARACTERISTICS OF PETROCHEMICAL INDUSTRIES AND FACTORS CONDITIONING THEIR DEVELOPMENT

United Nations Contre for Industrial Development

#### Introduction

Developing countries, especially those with abundant petroleum and natural gas resources, have shown increasing interest in the development of petrochemical industries. Market located petroleum refineries which are now being established in a number of countries also provide a basis for establishing petrochemical complexes. In addition, there are countries with an already existing organic-chemical industry, where oil and gas are being substituted for other traditional imputs, such as coal and raw materials of vegetable origin.

In the recent past, the petrochemical industry has shown a very high rate of growth in the world economy. It is a dynamic industry which supplies intermediate products for a number of other industries and provides substitutes for traditional materials such as steel, lumber, paper, natural fibres, soap, etc.

Of the approximately 1,000 petrochemical plants in existence more than 50 per cent are located in the United States and Canada, more than 200 in Western Europe, about 50 in Japan; the rest being distributed among all other areas. Nevertheless, new projects were at the end of 1963 distributed more evenly among the United States, Western Europe, Japan, and developing areas. The majority of the existing plants and projects in developing countries are still concentrated in Latin America and Asia, which account for 90 per cent of the total.

General characteristics of these industries are:

- (a) Product homogeneity and standardization;
- (b) Process continuity and stability;
- (c) High capital intensity;

(d) High proportion of skilled labour including technicians and scientists;

(e) Availability of alternative production processes and raw materials;

(f) High rate of technological change.

The high capital intensity, generally implies increasing returns to scale. Economies in capital investment range from 20 to 45 per cent, according to the type of production, when output is trebled. Economies in production costs also arise from reduction of unit costs in labour and capital. Thus, as a consequence, the relative share of raw materials in total cost rises with the increasing scale of production. Some examples may illustrate this point. For example, in the production of ethylene the capital investment in dollars per ton of ethylene may range from \$570 for a 10,000 ton/year capacity plant to \$250 for a 60,000 ton/ year capacity plant. In ammonia from natural gas, from \$179 per ton for a 36,000 ton/year plant to \$89 per ton for a 180,000 ton/year capacity plant. In carbon black, from \$300 per ton for a 10,000 ton/year plant to \$160 per ton for a 50,000 ton/year capacity plant, in polyvinyl chloride, from \$285 for a 6,000 ton/year plant to \$170 per ton for a 20,000 ton/year capacity plant.

Some examples may also illustrate the labour requirements in this type of industry. For example, a petrochemical complex for the production of synthetic rubber and other products in Argentina, demanding a capital investment of \$72 million, will give employment to 700 people, i.e., an average investment per worker of about \$100,000. A plant in Trinidad for the production of ammonium fertilizers employing 263 people will use only 22 unskilled labourers but will demand 145 technicians, engineers and scientists. Another plant to produce carbon black in a developing country uses only 45 per cent of unskilled labour, the rest being skilled workers, technicians, engineers and scientists. The same is true of an ethylene-polyethylene plant where skilled labourers, engineers and scientists account for 55 per cent of the total labour force.

The limitation in size of the market in many developing countries represents an economic barrier to the development of petrochemical industries. Exports of a good share of the output either to the international market or through regional arrangements to neighbouring countries could provide a solution. Some new developments in the transportation techniques for these products may originate important changes in the present pattern of location of petrochemical plants, as well as that of international trade. This applies to the transportation of liquid ammonia and ethylene in special ships. Although the number of export achievements from developing countries in this field is still very limited, some cases may be pointed out, for example in 1963, Trinidad and Tobago exported 115,000 barrels of olefin hydrocarbons to Great Britain and the United States; also 30,000 barrels of di-isobutylene and 12,000 barrels of aromatic hydrocarbons. Seventy thousand tons of ammonium sulphate and 23,000 tons of urea were also exported from Trinidad. Argentina also exported 3,000 tons of carbon black to Uruguay. Attempts are

already under way to establish new petrochemical industries in some developing countries in the framework of a regional market, Latin American Free-Trade Association (LAFTA) in Latin America is such an example.

#### 1. Historical review

For the purposes of this paper, the petrochemical industry is defined as that segment of the chemical industry producing chemical products from raw materials of petroleum origin.<sup>1</sup>

Petrochemical production is generally considered to have been initiated in the United States in 1919-20, with the manufacture of isopropyl alcohol. This was followed by the hydration of olefins leading to a cohols and to derivatives of alcohols already made from other sources, and the oxidation of olefins leading to the olefin oxides and their derivatives which were new chemicals not previously produced.<sup>8</sup>

Among the olefins, ethylene was the main building block, starting with ethylene oxide whose derivatives found application in the automotive industry; ethylene glycol as antifreezer and the glycol ethers in the new paints developed for automobiles.

The many demands imposed by the Second World War led to a tremendous expansion of the petrochemical industry in the United States. Whilst the growing demand of the automobile industry for automotive chemicals gave the initial impetus to petrochemistry, most other product lines today firmly based on petrochemical routes were also strongly stimulated by the requirements of the war period. The production of ammonia and nitrogenous fertilizers followed developments in the field of explosive production. War needs were also responsible for the development of synthetic rubber production to substitute for the natural product. The manufacture of promatics from petroleum, first toluene and xylene, afterwards benzene, also originated at this time because the growing demand could not be met from the traditional source, coke-oven tar. Then came new industries, mostly created after the war, which also obtained their raw materials from petroleum. These include synthetic fibres, plastics and detergents.

Outside the United States, petrochemical production did not really begin to develop until after the Second World War, but it has been growing at a very high rate since then, e. pecially in Europe and Japan. In addition, it appears now to be one of the most dynamic sectors in some of the developing countries.

Although petrochemical industries are still concentrated in the economically advanced countries, efforts at industrialization seem to have been paralleled in many developing countries with a high rate of investment in the petrochemical industry. Also, among the centrally planned economies steps have been taken recently toward increasing investment in the petrochemical sector. Many reasons have been suggested to explain such a trend. This paper will attempt to summarize some of the main characteristics and factors underlying the development of petrochemical industries, and furthermore explain the role these industries could play in advancing industrialization in developing countries.

#### 2. Distribution of petrochemical plants

More than 500 operating plants belonging to more than 200 companies were listed in 1963 as directly involved in petrochemical manufacturing in the United States; while about 65 plants were reported in Canada and more than 200 in Western Europe. Table 1 shows the world-wide distribution of petrochemical plants and projects in 1963.

Whilst the majority of the existing production capacity is concentrated in the United States and Europe, a good part of the projected installations belong to Japan and the less industrialized areas.

Among developing countries there has been in recent years, as mentioned before, increased investment activity in the petrochemical field. Table 2 summarizes data available for recent years on existing petrochemica! plants and projects in developing countries.

Up to last year more than 50 per cent of all the existing and projected plants were located in Latin America; most of the existing plants and projects being concentrated in three countries: Argentina, Brazil and Mexico. In Asia, India had the majority of the installed and projected plants.

Commiry or area	Existing plants (1)	Projected or under construction (2)	Ratio of projected to existing plants (2) : (5)
United States	511	67	0.13
Western Europe.	226	60	0.26
Canada.	62	13	0.21
Japan	52	43	0.83
Total, other areas •	82	72	0.88
Total.	933	255	0.27

SOURCE: The Oil and Gas Journal, Sept. 2, 1963.

· Centrally planned economies not included.

This information is, of course, only an indication of the investment activity taking place, since no accurate account of the capital involved is available. One important structural feature characterizing this investment in petrochemical plants in developing countries is that the majority of the existing and projected plants are for the production of ammonia and nitrogenous fertilizers, and only a few for the production of synthetic rubbers and fibres. Table 3 illustrates this point, showing that while ammonia and fertilizer plants were about one third of

<sup>&</sup>lt;sup>1</sup> In this context petroleum includes both oil and natural gas. <sup>8</sup> Richard P. Goldstein, The Petroleum Chemical Industry, 2nd edit., 1958, p. 10.

the total, plants for the production of elastomers and fibres accounted only for about 8 per cent of the total number.

Fertilizer plants rank first on account of the growing demand for nitrogenous fertilizers to increase agricultural productivity in developing countries, and the easy availability of the necessary technological "know-how", whilst the production of synthetic rubber and fibres, although not demanding higher capital investment, does require a more complex technology. Also, in many developing countries its development would imply substituting traditional industries sometimes based on domestic raw materials.

 
 TABLE 2. PETROCHEMICAL PLANTS AND PROJECTS IN DEVELOPING COUNTRIES-1961, 1962, 1963

		Plants			Projects		
	1961	1962	1963	196;	1962	1963	
Latin America.	26	36	48	30	35	28	
Asia and Far East	6	6	10	20	32	32	
Middle East.	1	2	2	3	6	6	
Africa		-	1	_	2	4	
TOTAL	33	44	61	53	75	70	

SOURCES: The Oil and Gas Journal, Sept. 4, 1961, 1962, and Sept. 2, 1965.

TABLE 3. PPTAOCHEMICAL PLANTS AND PROJECTS IN DEVELOPING COUNTRIES CLASSIFIED BY PRODUCT LINE----1963

			,	70	<b>in</b> ci			<b>.</b> .					 -	Plants	Per cen
Ammonia and	nit	ro	80	nc	vus	ſ	er	tili	ze	<b>rs</b>				41	32.4
Plastics											,			30	24.0
Synthetic rubbe	r.													7	5.5
Synthetic fibres														3	2.4
Onherst														42	33.3
Unspecified														3	24

SOURCE: The Oil and Gas Journal, Sept. 2, 1963.

 includes: Acetone, carbon black, sulphur, benzene, phtalic anhydride, toluene, solvents, det rgents, insecticides etc.

#### 3. Capital requirements

Manufacturing operations for the production of petrochemicals are rather capital-intensive. I his can be shown using different criteria, like average investment per production worker, relative share of capital cost in total unit cost, capital-output and capital-labour ratios etc., for comparing petrochemical industries with other industrial sectors.

#### AVERAGE INVESTMENT PER PRODUCTION WORKER

The following table shows data for some manufacturing industries in the United States.

TABLE 4. CAPITAL INVESTMENT PER EMPLOYEE, 1959

						United States dollars
Petroieum						63,000
Chemicals and allied products						23.000
Basic metals						19,000
Food and kincred products.						11,500
Transportation equipment						10.500
Textiles						

SOURCE: Manufacturing Chemists' Association, Inc.

#### CAPITAL INVESTMENT PER UNIT OF OUTPUT

While in 1940 the industry produced about 12 lb of petrochemicals per dollar invested, by 1945 physical output was 8.7 lb. per dollar inv. and 8.2 lb. in 1951, showing an increasing marginal capital output ratio. It was also estimated that the investment per barrel per day was \$12,500 in petrochemical plants and about \$4,300 in petroleum: refineries.<sup>8</sup>

The average investment per petrochemical plant was estimated at about \$12 million in 1957.<sup>4</sup> Further evidence is given by analysing data for 54 plants certified for fast tax write-off after the War by the Defense Production Authority of the United States. The average investment for petrochemical plants constructed by firms in the oil industry was \$9 million, while plants constructed by chemical companies averaged an investment of \$5.5 million. Plant investment ranged from \$2.5 million to \$38 million for oil company plants, while the plants erected by chemical companies ranged from \$1.5 million to \$19 million.<sup>4</sup>

Additional information on the value of net fixed assets to total tangible uet worth, as well as the working capital requirements of the industry, is provided in another United Nations Secretariat paper presented to this Conference.<sup>6</sup>

Furthermore, petrochemical technology is very dynamic and new techniques tend to render obsolete present plant facilities giving rise to higher capital costs per unit of output. This trend is being somewhat counteracted by increasing the scale of operations, and the rate of capacity utilization, and through the integration of petrochemical manufacturing facilities in industrial complexes. As a result, while the absolute amount of capital investment increases, the capital cost per unit of output declines. A more detailed discussion of the importance of scale economies in petrochemical manufacture is left for later in the part of this paper which deals with the cost structure.

<sup>&</sup>lt;sup>3</sup> Robert O. Law and Michael Piernonte, An Analysis of the Economics of the Patrochemical Industry (Bureau of Business Research, University of Oklahoma, 1954).

<sup>&</sup>lt;sup>4</sup> "Economics of Petrochemicals" in Advances in Petroleum Chemistry and Reforming, J. J. McKeita, ed. (New York 1960).

<sup>&</sup>lt;sup>a</sup> Ibid. It should be noted that benzene, sulphur, synthetic rubber and carbon black plants were not included among those considered for the fast tax write-off.

<sup>&</sup>lt;sup>6</sup> See chapter VII, A, I, below, Plnancing of Petrochemical Vantures in Developing Countries.

#### 4. Raw materials, intermediates, alternative routes and by-products <sup>7</sup>

Petrochemical industries are intermediate or "basic" industries, whose products are distributed as inputs through many other industrial sectors besides directly satisfying final demand. The petrochemical industry therefore has so far been concentrated in highly industrialized countrics. The principal exception is in the field of nitrogen fertilizers, which find a local market in all agricultural countries.

Two factors distinguish petrochemical operations in Europe and many other countries from American practice. In the first place, in the absence of natural gas, petrochemicals have to be made from imported liquid hydrocarbon fractions. Secondly, compared with America, many of the European countries are well placed on aromatic compounds as by-products from coal processes and the relative price structure does not make manufacture of aromatics from imported oil attractive.

Among the reasons for making chemicals from petroleum are, first, that one can make them mor echeaply from petroleum than from other raw materials, second, that there is an adequate supply of raw materials at a reasonably constant price.

Petroleum chemicals have tended to displace the older routes, based primarily on coal and vegetable matter. In addition to this competition between starting materials, one also finds, for the same reason of cost, competition within the petrochemical industry between different intermediates, such as between petroleum ethylene and petroleum acetylene.

The tremendous growth of petrochemicals has been due to a combination of 'wo factors; the displacement of older raw materials and the expansion of demand for those end-products based on petroleum chemicals as their raw material.

The main raw materials from petroleum for the production of chemicals are: natural gas, crude oil, refinery gases and various refinery-distillates and residues. Natural gas provides the basis for the manufacture of the lower aliphatic petrochemicals and for the production of carbon black and the derivatives from synthesis gas, notably ammonia, methanol and their end products.

The petroleum raw materials mentioned above are processed into various intermediates. The main groups are the olefins, aromatics, acetylene, and paraffins.

Of the lower olefins, ethylene is the key product. Propylene and the butenes are available from oil refinery operations at little more than fuel value. Ethylene is not obtained solely from waste refinery gases by straight separation, partly because there is not enough available, and partly because the concentration is too low. Therefore ethylene has to be made by operations specifically devoted to its synthesis—ad hoc cracking. It is usually manufactured alongside the chemical unit consuming it because storage and transport costs are high. The starting points for ethylene are ethane, propane and liquid hydrocarbons. Ethane and propane are available where ample supplies of natural gas exist in excess of the local demand for fuel. The small ethane and propane content of natural gas is extracted, which hardly affects the usage or value of the stripped gas. The cost is therefore the equivalent of methane plus the cost of extraction. At present there are only a few gas systems in the world carrying such a gas volume as to justify the expensive chemical plants for making and consuming the ethylene. Ethane and propane give only ethylene, so that there is no problem of finding outlets for co-products.

In less favoured countries, it is necessary to crack liquid hydrocarbons. Many of them have a naphtha surplus because there is more demand for heavy fuel oils than for gasoline, i.e., India, and even Europe. This inevitably gives propylene and butenes in an amount of the same order as the ethylene produced. It is necessary to provide outlets for propylene and the butenes in the chemical industry as ethylene alone cannot bear the whole cost of the cracking operation. The need to find profitable outlets for  $C_8$  and  $C_4$  olefins has to a certain extent been a limitation on the rate of growth of ethylene chemicals.

Highly industrialized countries are now well equipped with refineries and the propylene and butenes available in the refinery off-gases are usually more than sufficient for the foresecable demands of the chemical industry. The  $C_8$  and  $C_4$  olefin by-products of ethylene cracking plants are therefore worth no more than the alternative cost of  $C_8$  and  $C_4$  olefins in refinery gases.

In Western Europe before the post-war development of petrochemicals, ethylene requirements were met by dehydration of ethyl alcohol made by fermentation of imported molasses or from the ethylene fraction obtained in processing coke oven gas for the sake of its hydrogen and methane content for the synthesis of ammonia.

The method has been widely used in Western Europe but their increasing ethylene requirements have now to be met from oil, since the amount produced is limited by how much coke oven gas is processed. Dehydration of ethyl alcohol is becoming obsolete. The same is true of other areas like India and the USSR, where ethyl alcohol from vegetable origin was widely used as a chemical raw material.

With regard to aromatics, petroleum has displaced coal as the dominant source, and it now exceeds all other raw materials as a source for benzene, toluene and xylenes (BTX). These aromatic chemicals are the basis for the production of phenol, cyclohexane, aniline. styrene, dodecyl-benzene, etc., which in turn are the key components for the production of synthetic resins, plastics, synthetic fibres, dyestuffs, synthetic detergents and pesticides. Benzene, toluene and xylenes are separated from pyrolisis gasolines by purification followed by extraction in order to separate BTX-cuts from the nonaromatics of the same boiling range. The potential availability of toluenc from BTX fractions is between five to seven times that of benzene, which is far from matching the proportion in which they are demanded. Several processes have been recently developed to balance the production of aromatics by converting surplus toluene

<sup>&</sup>lt;sup>7</sup> This section draws heavily on material contained in R. F. Goldstein, The Petroleum Chemicals Industry (2nd edit., 1958), chep. XXII.

to benzene. There remains the problem of separating the xylenes ( $C_s$  aromatics), which presents difficulties because they have close boiling points. The separation is done by distillation, superfractionation and crystallization.

Acetylene is the other major building block for the production of petrochemicals. The major outlet for acetylene is PVC, but it shares this market with ethylene which has been gaining at the expense of acetylene because of its lower price. Acetylene is obtained from calcium carbide, natural gas or naphtha. Due to rising costs of coal and electric power, the carbide-based acetylene process is now being displaced even in Europe, and it is likely that future expansion of acetylene capacity will be based on natural gas and naphtha as raw materials.

Paraffins have gained in importance in the last years as raw materials for biodegradable detergents. They are separated from petroleum distillates by a modern process of selective adsorption utilizing so-called "molecular sieves".

#### 5. Petrochemical processes and equipment

Most of the techniques which are used in petrochemical manufacture come from petroleum technology, and several are well known in a more general sense. Amongst the processes of importance in petroleum chemical manufacture are:<sup>8</sup>

#### (a) Distillation

This is a technique of separation which makes use of the difference in boiling point of the components in a mixture. It is effected in a column containing a series of horizontal perforated plates or trays spaced inside. The aim is to carry the most volatile component of the mixture away in the vapour phase from the top of the column, and to draw off the least volatile component as a liquid from the bottom. Side streams may also be taken from almost any point up the column. The term distillation is properly applied only to those operations where vaporization of the liquid mixture yields a vapour phase containing more than one constituent. Where the vapour from a liquid mixture or solution contains only one component, the process is described as evaporation.

Distillation may proceed at atmospheric pressure, under high vacuum, or at elevated pressure, in accordance with the specific requirements of the separation.

In order to assist the separation effect, it is sometimes necessary to modify the process of simple fractional distillation, e.g. by adding additional components. This results in such operations as steam distillation, extractive distillation (distillation in the presence of a solvent which becomes the least volatile component of a mixture), and azeotropic distillation (distillation in the presence of a solvent which becomes the most volatile component of a mixture).

#### (b) Solvent extraction

This is the separation of component or components of a mixture by the use of a liquid with selective solvent characteristics. This operation is used, for example, to separate aromatics from parafiles.

#### (c) Crystallization

By allowing a component to form crystals from solution, or from a moltan mixture, the solid crystals can be separated by filtration or cantrifugal separation from the other components.

#### (d) Absorption

This process is a form of solvent extraction. A component of a gas or vaporized mixture is separated by selective absorption, usually in a liquid solvent.

#### (c) Adsorption

Certain highly porous materials (e.g. activated charcoal, silicagel) have the power of condensing on their surfaces large amounts of vapours. Where this adsorption can be operated selectively, it represents a technique for the separation of one component from a mixture.

#### (f) Cracking

By this process large hydrocarbon molecules are broken down into molecules of lower molecular weight. This is achieved in the absence of air, by high temperature alone (thermal cracking or pyrolysis) or by a combination of high temperature and catalytic activity. Thermal cracking in the presence of steam is a modification normally designed to give high yields of unsaturated gases.

Amongst the iow molecular weight products of cracking are the lower paraffins and clefins, which represent major raw materials for petrochemical production.

#### (g) Reforming

Gasoline is subjected to thermal or catalytic reforming to modify the molecular structure of its components, so that the final product has a higher anti-knock rating. Reforming is more commonly carried out catalytically and in the presence of hydrogen.

The term reforming is also used more loosely in connexion with a variety of hydrocarbon reactions (e.g. the methane-steam reaction) which will form synthesis gas or town's gas.

#### (h) Alkylation

This term is used to describe a reaction in which a straight-chain or branch-chain hydrocarbon group (called the alkyl group) is united either with an aromatic molecule, or an unsaturated hydrocarbon group to form a new complex molecule. This process is commonly used in the production of alkylated aromatic compounds. The reverse reaction is called dealkylation, and has been recently applied in the production of benzene from toluene.

#### (i) Isomerization

This is a process designed to induce a rearrangement of atoms within a particular molecule. In the petroleum field it is commonly applied to the conversion of a normal paraffin to the isoparaffin. Isomerization is of significance in the application of catalytic reforming techniques to aromatics production.

#### (j) Polymerization

Polymerization is the process by which molecules are combined together to form larger, and more complex, molecules of the same empirical formula. The single molecule is called the monomer, and the combined molecule the polymer. The product may be described as a dinner, for a combination of two monomer molecules; the trimer and tetramer representing respectively combinations of three or four monomer molecules.

#### EQUIPMENT REQUIREMENTS FOR PETROCHEMICAL PLANTS

As we have seen the manufacture of petrochemicals involves a number of continuous physical operations such as distillation, extraction, filtration, mixing/pumping, etc., during which no change in chemical structure takes place.<sup>8</sup> The equipment utilized is similar to that used in

<sup>&</sup>lt;sup>8</sup> Based on A. Lawrence Waddams, *Chemicals from Petroleum* 1962, pp. 11-14.

<sup>\*</sup> This characterization of the petrochemical operations is based on material from Sheil International Petroleum Co. Ltd., The Petroleum Handbook, (4th edit., 1959), p. 272.

oil processing operations, but many items are generally smaller, since the volume handled is generally less than the output of an oil refinery.

#### Some additional aspects are:

(a) The chemical conversions very often demand strict control of temperature, pressure, reaction velocity, etc., and these factors determine the dimensions and construction of the equipment;

(b) Being in most cases continuously operating plants, processes may be controlled by means of automatic instruments;

(c) Since many of the chemicals are corrosive, stainless steel is widely used, and also glass and plastics for the lining of vessels.

As an indication of the equipment needed for typical petrochemical production, table 5 lists the joint requirements of a group of petrochemical plants.<sup>10</sup>

TABLE 5. EQUIPMENT REQUIREMENTS FOR PETROCHEMICAL PRODUCTION

	Waleht	Ce	N
	(Tone)	(Thousands of dollars)	Per cen
Storage tanks	11 <b>,700</b>	4,642	9.1
Pressure vessels.	6,342	6,344	12.4
Heat exchangers	2,100	3,775	7.4
Furnaces.	1,964	1,920	3.7
Pumps and drivers		2,313	4.5
Compressors and drivers.	•	4,880	9.5
Valves	3,300	5,112	10.0
Piping	9,960	7.668	15.0
Structural steel	3,315	1,599	3.1
Instr. and Cont. valves	•	1,590	3.1
Steam generators	1,950	1,544	3.0
Turbo generators		2,888	5.6
Electric distribution	•	4,242	8.3
Miscellaneous	869	2,7_3	5.3
TOTAL	41,500	51,250	100.0

SOURCE: ses foot-nots.

• Not available.

It can be seen from the data that some of the major components of the cost and steel weight consist of rather simple equipment like piping, valves, storage tanks and structural steel which could be produced in many developing countries. At later stages of development the construction of more sophisticated pieces of equipment like compressors, pumps and generators could be added.

The co-operation of constructors, licensors, foreign investors, and engineering companies, is necessary in order to facilitate local supply of such equipment since provisions have to be made during the mechanical design stage to adapt specifications and drawings to the raw materials and construction facilities available in each country.

#### 6. Technological change-research and development

The petrochemical field is continuously undergoing technological change. A substantial part of technological change now originates in organized research and development (R&D), and we shall see that chemical oriented industries have high research intensity as measured by different criteria.<sup>11</sup>

Under the impact of technological change, new products and processes are continuously replacing old ones, and new uses are discovered for existing products. Although a good part of the technology in use has been developed in the United States, the European contribution has been substantial and Japan is now also becoming an originator of new technology.<sup>18</sup>

The fast rate of technological change characteristic of this industry has important implications for developing countries starting petrochemical industries, *inter alia* in the following aspects: selection of products to be produced; evaluation of possible raw materials, analysis of alternate routes, processes and equipment, utilization of by-products, and the integration of production facilities in petrochemical complexes.

Although the problem for developing countries is, in the long run, to catch up with the industrialized countries on the generation and development of new technology, in the initial stages of industrial development the key question is how to effectively utilize the "best" available technology for each purpose and condition. This approach can be well illustrated by referring to the tremendous growth experienced by the Japanese petrochemical industry during the last ten years on the basis of imported foreign technology. Mexico also provides a similar example.

Special skills and "know-how" are embodied in the three technical phases of constructing petrochemical production facilities: process design, mechanical design and construction. While process design would seldom be available from local sources, in many developing countries there is a pool of engineering and technical skills competent enough to undertake locally most of the mechanical design and construction engineering. The

<sup>&</sup>lt;sup>10</sup> Estimates given in United Nations, "The manufacture of basic industrial equipment in Argentins. II. The production, transport and refining of perroleum and natural gas: The petro-chemical industries" (IJCN.12/629/Add.1); and based on the joint equipment requirements of an SBR excitatio-rubber phast, a physicitytians phase and a plant to predice phosed from beauses, involving a total capital investment of about \$100 million.

<sup>&</sup>lt;sup>11</sup> As examples: percentage of sales income spent in  $\mathbb{R} \triangleq D$ , and properties of  $\mathbb{R} \triangleq D$  employees in total employment (see table 7).

<sup>&</sup>lt;sup>16</sup> Among the most important petrochemical products which originated in European chemical technology are: synthetic ammonia, synthetic desergents, polyuretheses, polyvinyi acetate and alcohol, polyvinyi oblocide, sylon-G, synthetic rabbers: BUNA-N and BUNA-B, and oto-alcohols in the Pederal Republic of Germany; polyethylene and polyester fibres in the United Kingdom; acrylettes in the United Kingdom and the Pederal Republic of Germany; synthetic fibry alcohols and acids in the UBIR and the Pederal Republic of Germany.

same is true of the engineering and construction facilities required for the production of a major portion of the plant equipment.<sup>13</sup>

It is also important to realize that the early utilization of domestic skills is a prerequisite for the formation of the engineering cadres essential to further petrochemical development. Special attention should be paid to the creation of a modern chemical engineering force which could first operate and muintain plants of imported process "design", develop specifications for mechanica! design using domestic equipment, and later on deal with adaptations to local raw materials and operating conditions.<sup>14</sup>

The attention paid in the United States to chemical engineering as opposed to basic chemistry in Europe is probably one of the explanations for the relative technological leadership maintained in this field by American industry, despite the fact that the basic work of chemical synthesis was done in many cases in European laboratories. This emphasis on chemical engineering was also coupled with the application of sound process-economics aimed at supplying a large and growing market.

Thus, in considering the production of petrochemical products, mechanisms of critical appraisal should be built in to reflect—together with basic economic considerations—the major technological trends in the field. The accelerated rate at which new products and processes are developed, together with the reduction in the economic life expectancy of existing products and markets, makes this imperative for developing countries.

Research and development in industry in the United States has been well analysed in recent studies by the National Science Foundation<sup>16</sup> and the National Industrial Conference Board.<sup>16</sup> The information provided here draws heavily on these two publications and since no similar sources were available for other countries most of the conclusions will be only valid for the American industry.

Industrial research and development is now running in the United States at a \$16 billion level of expenditure a year, with industrial research and development absorbing about three-quarters of all the resources presently being invested in research and development.

Measured in terms of manpower there were in 1960, 1.1 million research workers representing 16 per cent of the total employed labour force. Of these about 400,000 were research and development scientistr and engineers and 700,000 supporting workers such as technicians, craftsmen, maintenance and clerical personnel. Of the total of about \$10.5 billion spent in 1960 for research and development by industry. 11 industrics accounted for 95 per cent of the total.<sup>17</sup> Among these industries, chemicals and allied products ranked third in research and development performed costs with about \$1 billion and 7.2 per cent of the total for the United States, and petroleum refining and extraction seventh with about \$300 million and about 2.1 per cent of the total for the United States.

A ranking of industries based on privately financ-d research and development is led by chemicals and allied products, and electrical equipment and communication industries, each with 18 per cent of the private total, followed by motor vehicle producers with 14 per cent and machinery manufacturers with 13 per cent.

With regard to the distribution of research and development personnel by industry, chemicals and allied products ranked fourth with 9.3 per cent of the total after transportation equipment with 40.1 per cent, electrical equipment and communications with 20 per cent and machinery with 12 per cent. Petroleum refining and extraction had about 3 per cent of the total number of research and development employees. As an additional feature, chemical companies were the most intensive users of outside research, followed by motor vehicles, metal producers and machinery manufacturers.

With regard to the composition of research and development work by stage of research process, in 1960 chemicals and allied products had 46 per cent of industrial research and development in development, 42 per cent in applied research and about 12 per cent in basic research while petroleum refining and extraction had about 41 per cent in development, 40 per cent in applied research and 19 per cent devoted to basic research. Chemicals, machinery and motor vehicles each absorbed between 5 per cent and 8 per cent of all funds for research and development work in the industry. Industrial chemicals, plastics and man-made fibres constituted the most important product fields of chemical research.

In the petroleum industry, petrochemicals were estimated to account fcr only about 15 per cent of oil companies' revenues in 1960 but absorbed 20 per cent of research and development outlays.<sup>18</sup>

There seems to be a positive relationship between research and development expenditures and performance criteria such as growth, profits and productivity. One indication of this is given by correlating the level of research spending relative to sales with the proportion of sales from new or improved products. For example, chemicals had a total of 4.3 per cent of research and development spending as percentage of industry net sales

<sup>&</sup>lt;sup>18</sup> See United Nations/ECLA, The Manufacture of Industrial Machinery and Equipment in Latin America-I-Basic Equipment in Brazil (United Nations publication, Sales No.: 63.II.G.2) and United Nations/ECLA, "The manufacture of basic industrial equipment in Argentian. II. The production, transport and refining of petroleum and natural gas: The Petrochemical Industries" (E/CN.12/629/Add.1).

<sup>&</sup>lt;sup>14</sup> Since continuous operation is essential for these industries, it is very convenient to rely on domestically available equipment and parts to prevent harmful breakdowns or oversized inventories.

<sup>&</sup>lt;sup>16</sup> National Science Foundation, Research and Development in Industry in 1961.

<sup>&</sup>lt;sup>36</sup> Nestor E. Terleckyj and H. J. Halper, *Research and Develop*ment: Its Growth and Composition (The National Industrial Conference Board, Studies in Business Economies No. 82, 1963).

<sup>&</sup>lt;sup>17</sup> These industries were: aircraft, electrical equipment and communications, chemicals, machinery, motor vehicles, professional and scientific instruments, petroleum refining and extraction, primary metals, rubber products, fabricated metal products and food and kindred products.

<sup>&</sup>lt;sup>14</sup> Wall Sweet Journal, October 18, 1961. Cled in Nester E. Terleckyj and H. J. Halper, Research and Development: By Growth and Composition, p. 54.

in 1958, and the sales of products not in existence in 1956 as a percentage of 1960 sales was 16 per cent. In rubber, with 3.5 per cent of research and development spending relative to net sales, sales of new products were 17 per cent of 1960 nct sales.

Research and development work seems to be concentrated in large companies. In 1960 companies with 5,000 or more employees accounted for 86 per cent of the total performance cost of industrial research. In addition, the top four performers in manufacturing accounted for 22 put cent of the total research and development cost, the top 20 for 54 per cent and the top 300 research and development performers for 92 per cent of all expenditures for industrial research and development.

As measured by the proportion of total research and development cost, the percentage of research and development work performed by the four leading research performers ranged in 1960 from 88 per cent in motor vehicles and 86 per cent in the rubber industry to 48 per cent for petroleum refining and extiaction, 60 per cent for industrial chemicals, 52 per cent for other chemicals, to a low of 31 per cent for paper and allied products.

Since research and development activities are concentrated among leading companies, and represent one important key to company growth, research and development may result in increased concentration and reduction of competition. There are also probably economies or scale in conducting research and development, although there is not enough factual evidence on this matter.

In order to compare the intensity of industrial research for several selected industries, table 6 is included indicating different ratios like research and development costs as percentage of sales, research and development employees as percentage of total employment, and professional employees as percentage of total employment.

There is a tremendous range of variation of research intensity for individual product fields. In 1958 applied research and development cost as percentage of value added was about 40 per cent for communications equipment and electronic components, 25 per cent for office and computing machinery, 19 per cent for aircraft, 15 per cent for plastics and synthetic fibres, 7.4 per cent for petroleum refining and extraction, 5.5 per cent for agricultural chemicals, 4.7 per cent for industrial chemicals and 1.3 per cent for rubber products.

In analysing the trend of research intensity during the 1950s, it is seen that during the 1950s cost of research and development increased substantially in relation to sales in most industries. For example, for professional and scientific instruments it went from 5.8 per cent in 1951 to 7.3 per cent in 1957 and 8.6 per cent in 1960, while in machinery it went from 1.5 per cent to 4.2 per cent and 4.3 per cent, respectively, and in chemicals and allied products from 2.5 per cent to 3.5 per cent and 4.2 per cent, and in petroleum refining and extraction from 0.6 per cent in 1951 and 0.8 per cent in 1957 to 1.1 per cent in 1960. Again, a factor influencing the relative scale of research and development activity is the company size. The research sales ratio appears to be positively correlated with company size. In industrial chemicals the ratio of research and development cost as percentage of sales was 5.3 per cent for all companies and 2.7 per cent for those companies with fewer than 1,000 employees. In rubber products it was 2.1 per cent for all companies and 0.9 per cent for those employing fewer than 1,000 employees.

Finally, if we relate research expenditures to total capital investment we see that research and development

TABLE 6. COMPARISON OF VARIOUS RESEARCH INTENSITY RATIOS FOR SELECTED INDUSTRIES IN THE UNITED STATES OF AMERICA, 1958

	.AH 00	and community		Companies consisting research and development			
Budhutry	Total R & D coli au per coli of adas			Total & & B 640 65 per 540 67 adas			
Total, all industries	2.3	4.0	1.4	3.8	1.7		
Aircraft and parts	16.8	24.1	7.3	17.7	2.6		
communications	8.9	10.2	3.7	10.5	3.3		
instrumente	6.4	9.2	3.8	7.5	3.9		
Chemicals and allied products.	3.4	7.2	3.3	3.4	3.1		
Mashinery	2.9	S. j	1.0	3.6	2.3		
	1.0	3.7	1.6	1.1	1.0		
Petricated metal products	0.7	1.1	0.5	1.4			
Rabber products	0.6	1.3	0.6	1.8	1.5		
Primary motals	6.6	0.5	64	0.3	6.9		
Food and bladed products .	0.1	6.4	6.2	<b>A</b> .)	ě.		

Bannati: Mester R. Techningi and H. J. Halpen, Appenred and Development: By Grouth and Spapealites p. 18.

has become an increasing part of total investment. In 1960, privately financed research and development as percentage of total plant and equipment outlays, plus privately financed research and development, was 32 per cont in the chemicals and allied products industry, 26 per cent for rubber and 9 per cent for petroleum, while the average was 20 per cent for all industries. The general trend has been towards increasing company spending for research and development as a percentage of combined research and development and plant and equipment spending in the United States from 15 per cent in 1953 to 21 per cent in 1960.

The research and development characteristics in these industries may thus be summarized as follows:

(a) The chemical and allied products industry has istently reported the greatest amount of company

financed research and development work in non-manufacturing and manufacturing industries. In 1961 chemical companies financed \$877 million worth of research and development (see table 7).

(b) The chemicals and allied products industry accounted in 1961 for the greatest portion of the total company financed outside contracted research and development work, amounting to \$32 million.

(c) The concentration of research and development funds in selected companies in individual industries was greatest in motor vehicles and other transportation equipment, non-ferrous and other metal products, and rubber products. In industrial chemicals the first four companies accounted for 60 per cent of the total and the first twenty for more than 90 per cent of the total, while in petroleum refining and extraction the first four com-

TABLE 7. COMPANY-PRANCED BERARCH AND DEVELOPMENT, BY INDUSTRY, UNITED STATES OF Anna 1957-61

Budinetry			···· ·			Million o	f dalla	N			
		196	I		-				-	·	1967
Те	TAL	4,63	1	4,	510	4,	<b>85</b> 5	3,	<b>\$\$</b> 3	3	.459
Pood and kindred products		106		97							
rentings and apparel.		•						73 17		7	-
Lumber, wood products, and fe	-101							1/		1	2
heper and allied products		63						42		11	
Chemienie and allied products		877		833		700		-		X	
Industrial chemicals		5	61		546		-				• • • ••
Drugs and modifies		1	92		173		144		458 137		440
Other chemicale.		1:	24		113		110				114
visebum rolining and entraction		206		204		257	114	231	<b>101</b>		<b>11</b>
Lubber products				12		73		63		- 201	
tone, elay and gines prochests.		95		93							
vimery motale	•	151		140		131		114			
Primary ferrous products.		9	Ŋ		95	121	-	1 14	~		_
Non-forrow and other motel p									76		•
		5	IJ		54		51		14		
ubrimted metal products .				85	•••	76	31	79	38		•
hebinary .		610		361		334		-			
	-									-	
		871		815		671		627			
Communication equipment as	nd –					••••		•6/			
electronic components		39	•		341		200				
Other electrical equipment		47	2		474		383		247		
Alan anote in the state of the	<b>B</b>				••••				300		•
tion equipment.		636		679		625		548		-	
	•	392		401		384					
								_			
Sejantific and sumbrained		242		196		172		157		144	
And the second sec											
	•	8	1		79		64				-
and other burners and and and	R,								-		
and antiger more induction	•	130	)	1	21	1			97		
ner unserentet in ing industries	•	<b>62</b>		56	-	129		126	71		
		6									

nal Inivana Par b: Maste arch and Development in Industry, 1961, p. 12. a. A

it analytic separately but included in total.

a for this industry for the yours 1997-07 are included in the "other manufacturing and

TABLE 8. PUNDS FOR TOTAL R & D PERFORMANCE AS PERCENTAGE OF NET SALES, IN MANUFACTURING COMPANIES PERFORMING REMARCH AND DEVELOPMENT, BY INDUSTRY AND SIZE OF COMPANY, UNITED STATES OF AMERICA, 1957-61

industry and size of company	1	961	1	969	1	9.99	1	958	1	957
Тота	L 4.	4%	4.	4%	4.	1%	4.	0%	3.	7%
Foot and kindred products	. 0.3	موديرة مستسلان	0.4		0.3		0.3			
Tentiles and apperet.	84		0.6		0.4		0.3		0.3	-
Lumber, wood products, and furni			0.0		<b>U.</b> 4		0.4			•
ture	. 0.5		0.6		0.4		0.5			_
New and allied products	07		0.7		0.6		0.3			•
Chemiesi and allied products.	. 4.6		4.5		3.9		4.3		0.7	
Industrial chemicals		5.5		5.8		4.9	4.3		3.5	
Drugs and modicines	_	4.7		4.6		4.2		5.2		4.5
Other electricals.		2.8		2.3		1.9				
virsion rolining and extraction	. 1.6		1.1	<b>.</b>	1.0	1.9		1.9	• •	1.
Labber products	2.2		20		2.0		0.9		0.8	_
tons, elay, and glass products .	1.0		1.7		4.0	•	2.0			
Timery metals	0.8		0.5		0.5	-		•		
Primary forrous products.		0.7		0.6	0.3	••	0.7	• •	0.5	
Non-ferrous and other metal pro		<b>v</b> . /		U.Q		0.5		0.6		•
duete	-	i.0		1.1						
obviouted metal products	11	4.9	1.4	1.1		0.9		0.9		•
lachinary	4.4		4.6		1.4		1.6		1.5	
setrical equipment and communi	-		7.9		4.3		4.4		4.2	
estions.	10 A		10.4							
Communication equipment and	1414		1844		10.7		12.9		11.0	
electronic components		12.4								
Other electrical equipment		3.0		12.9 9.2		12.4		12.4		11.0
later vehicles and other transports	_			9.4		9.5		•		
tion equipment	2.9				• •					
iversit and missiles.	24.2		1.0		3.3		41		2.9	
relational and salentific instruments	7.3		22.9 7.6		28.6		18.7		18.9	
Scientific and mouhanishi massur-			7.0		7.9		7.8		7.3	
ing instruments.		9.2								
Optical, surgioni, photographic and	r	7.4		10.8		11.0		10.1		9.7
other instruments.		61								
ther industries	1.4	<b>W</b> 1		5.6		5.8		6.2		<b>5.7</b>
writution by size of company	1.49		1.3		1.3		1.3		•	)
(based on member of employers) :										
Les then 1,000.	2.0				• •					
1,000 to 4,000			2.0		2.1		1.5		2.0	
	11		22		1.8		2.5 •		2.1 •	
	5.2		<b>\$1</b>		4.8		5.8 •		44.	

Source: National Science Presidentia, Research and Development in Judnery, 1961, p. 40. • Not evaluable expansion but included in total. • Battes for this industry for the years 1997-30 are substal in the "other industries" group.

· Supports data for comparise with 5,000 or more exployees and for comparise with 1,000 to support originates over comparise with 5,000 or more exployees and for comparise with 1,000 to a province of the second of the National Balance Franchises for 1997 and 1998. Revisions of a & D emblished by the United Balance Duranes of the County for these years did not yield expensive data for comparise in these data groups.

penies assounted for more than 50 per cent and the first 7 per cent basic research, 20 per cent applied research, for 94 per cent, and in rubber companies the and 73 per cent development. Seet four assounted for 36 per cent and the first treasty (a) Chemicals, escent dram and medicines, she for 96 per cent.

(d) When considered according to the character of the remark and development work, the chaminis and alled predents industry devoted consistently from 1957 to 1961 restances and any devoted consistently from DDF to area more funds to basis records them any other industry. The distribution was: industrial aboution 13 per cost basis records, 30 per cost applied records, 50 per cost The distribution were industrial channels 12 per cast basis reasoned, 30 per cast applied reason, 50 per cast development: for persives coloring and extraction----16 per cast basis reasond, 42 per cast applied reasons and 42 per cast development; and for other predents----

(e) Chemicala, encept drugs and modicines, sho realised among the major contributors to applied research and development and speat about \$750 millions in applied research and development, the main folds being plastic materials and synthetic fibres and industrial inorganic and organic chemicals.

(f) Funds for total research and development as presentage of not miles were in 1961, 5.5 per cent for in-dential chamicale, 1 per cent for petrolouse relating and extraction, and 2.2 per cent for rubber products (see table 6). When considering only company functors research and development, the percentage of net sales was 4.4 per cent for industrial chemicals and 1.5 per cent for rubber products in 1961.

(g) The chemical industry employed as of January 1962, 34,000 scientists and engineers, ranking third in employment of scientific personnel, after aircraft with 94,000, and electrical equipment and communications with 72,500; while petroleum refining and extraction employed about 9,000 and rubber products 5,000. So chemicals and allied products employed about 11 per cent of the total force of scientists and engineers, and the three industries ranking first accounted for almost three-quarters of the total number of scientists and engineers in industry.

(h) With reference to total employment in industry, comparing with an average of 28 scientists and engineers per 1,000 employees for all industry, industrial chemicals had 42 per 1,000 employees and petroleum refining and extraction 17, and rubber products 20. Again, chemicals ranked third after aircraft with 101 per thousand employees, and electrical equipment and communications with 52 per thousand employees.

#### 7. Cost structure

#### ECONOMIES OF SCALE 19

Scale economies can be classified in several ways, the most useful of which is perhaps the distinction between economies internal to the plant and economies internal to the firm but external to the plant. Both categories can be further divided as due to "technical" factors and "economic" factors, although intraplant economies are mostly of a technical nature.

For the purpose of illustrating the notion, the main types of economies internal to the plant are briefly listed below:

(a) Large-scale production is often necessary for the optimum use of various kinds of indivisible equipment. Thus, as production increases beyond a given "threshold", costly equipment can be economically used;

(b) For various types of equipment cost is a function of surface, while output is a function of volume (i.e., tanks, pipes, etc.); for these types of equipment, therefore, cost increases less than proportionately with the increase in capacity;

(c) Greater production permits the use of advanced technological processes that need specialized equipment, greater capital "depth" or assembly-line methods;

(d) The cost of large-scale transactions increases less than proportionately with the increase in volume transacted; the phenomenon is well-known, and concerns the savings derived, for instance, from large-scale shipping, handling or storing; (e) As output increases, the need for invintory holdings as buffer protection against random market fluctuations increases less than proportionately. More precisely, statistical laws are such that in most cases the optimum safety inventory holding varies in proportion with the square root of the volume of sales. Of course, this principle operates not only with reference to inventories, but also with reference to all buffer stocks needed against random variation in general, such as the holding of cash balances for purposes of liquidity, and spare parts and repair facilities;

(f) A larger output usually implies a significant reduction of the average cost of a number of "overhead" activities, such as product design, production planning, quality control, research and development, etc;

(g) Finally, a larger size makes possible a greater specialization of workers, with consequent increases in productivity and reduction of unit labour costs.

Although it can safely be assumed that these factors are present, to some extent, in all industries, their economic relevance varies greatly among industries and among plants. There is some evidence in favour of the hypothesis that scale economies operate only until a given production limit is reached, although, to be sure, that limit is beyond present capacity in a number of industries and in most countries.

There is a general consensus that the economies external to the plant are less important than the former. Bain has shown in 1956 (working on 1951 data) that for several products (including steel, cement and soap, among others) the economies due to extra-plant factors do not exceed 5 per cent of unit cost. There is, however, some reason for stating that in recent times the significance of this type of economy has increased, owing to a greater emphasis on management rationality and organization.

The main types of such economies are:

(a) Those arising from the integration (vertical or horizontal, depending on the structural characteristics of the industry concerned) of plants, operations, functions of staff and management;

(b) Those arising from a degree of monopoly power, such as the greater profit implied in the possibility of securing "safe" market outlets;

(c) Those arising from a degree of monopsony power, i.e., the securing of better terms in the acquisition of materials and labour, and of casier credit terms in the borrowing of investment or operating funds.

Except for the first type, these factors are "economies" only in 30 far as the single firm is concerned, for, macroeconomically speaking, they do not usually entail any reduction in input-requirements.

Not only the quantitative impact, but the very existence of extra-plant economies depends on the characteristics of the industry considered. In some sectors (e.g. the automobile industry), large-scale management often entails a relevant reduction in average cost, while in others scale diseconomies may even set in, due to inefficiency or to unsuitability of integrated administrative operations to the firm or the industry in general.

<sup>&</sup>lt;sup>10</sup> The main references used are: Bela Balassa, The Theory of Economic Integration (Irwin, 1961); E.A.G. Robinson, The Structure of Competitive Industry (University of Chicago Press, 1950); J. S. Bain, Barriers to New Competition (Harvard University Press, 1956). Detailed foot-notes are not included because only the general information from the above publications has been used.

TABLE 9. ECONOMIES OF SCALE IN CAPITAL INVESTMENT FOR SELECTED PETROCHEMICAL PRODUCTIONS

Produci	O <sub>1</sub> Reference level of output (ion)	K. Capital investment (\$/ton)	a Capital Jactor	Economies in K investment <sup>b</sup> %	O, capacity range (ton/year)
Isopropyl alcohol	6,000	242	0.5	43	2,000- 30,000
PVC	6,000	285	0.55	38	2,500- 40,000
Butadiene	10,000	600	0.59	38	5,000- 60,000
Carbon black	10,000	300	0.58-0.60	37	4,000- 30,000
Ethylene (gasoline).	10,000	570	0.54	35	10,000- 60,000
Urea	33,000	85	0.67	31	16,000-165,000
Acetylene (gas)	13,600	465	0.67	30	10.000-45.000
Styrene	10,000	280	0.67	23	5,000- 50,000
Polyethylene (high pressure)	8,100	492	0.87	22	6,000- 12,000
Ammonia	36,000	139	0.73	22	18,000-180,000

SOURCE: United Nations/ECLA, La Industria Química en América Latina, 1964, annex XVIII, table A and p. 295.

• valid in the capacity range 
$$O_1$$
 to  $O_2$ .

• Equal to 
$$\frac{K_0}{K_0} \times 100$$

This brief review of the notion of economies of scale will help to show how the size of the plant and the level of output must be very large in an industry where scale economies have a primary role. Thus, if the cost-saving factors are to be exploited, a large investment is needed both to implant new facilities of economic (i.e., very large) size, and to operate them at an acceptable level of output.

Some illustrative data on scale economies in capital investment and production costs for selected petrochemicals is given in tables 9 and 10 based on engineering estimates and for technology, raw materials and capacity range as indicated in the source. An examination of these tables shows that economies in capital investment range from 22 per cent to 45 per cent. There are also economies in production costs arising from the reduction of unit cost in labour and capital, while raw materials and services are assumed to be proportional to output.

There is a great range of variation between the different petrochemicals examined, especially between products with a considerable amount of processing like plastics and resins for fibres, and basic intermediates, obtained by one or two processing steps from oil or gas, like ammonia and ethylene. The economies in production costs vary from no more than 10 per cent for the first group, to 15 per cent to 40 per cent for the last while output is increased by three to five times.

Another conclusion concerns the sensitivity of scale economies to output. Largest economies are achievable at the low and medium size capacity range while after large capacities they tend to disappear. This is generally due to technological indivisibilities and size constraints. Accordingly, developing countries being in most cases characterized by rather small domestic markets could still reap a good part of the potential scale economies while operating at a medium size capacity range.

Finally, it should be emphasized that the problem posed to the developing countries by the existence of scale economies is a two-sided question. On the one hand the

absolute level of capital investment required to construct and operate large-size (i.e., economic) plants is rarely available to developing countries, and especially the foreign exchange part of it. On the other, the higher the amount of capital invested, the lower tends to be the capital cost per unit of output, and the higher the share in unit cost of raw materials. As an example, while an ethylene plant producing 10,000 ton/year will have in its unit production cost 46 per cent of capital cost and 32 per cent of raw material cost, a 60,000 ton/year will have only 36 per cent of capital cost and more than 50 per cent of raw material cost. This has definite implications for developing countries in a position to exploit their potential comparative advantage in petrochemicals with a high percentage unit cost of raw materials or energy.

#### COSTS AND COMPETITION

In a relatively recent study made by the National Industrial Conference Board so the experience of United States firms manufacturing abroad was surveyed to find out which manufactured goods can at present be competively produced abroard and by whom. The study reports on recent trends in comparative international costs and provides information on productivity, profit margins, fringe benefits, etc. Chemicals and allied industries were among the industries included, and accounted for 25 per cent of the total number of comparisons made. Also, rubber products were included (about 7 per cent of the comparisons). Although most of the comparisons were made with industrialized areas, which accounted for about 60 per cent of the total, the study also includes some relevant material referring to developing countries, mostly in Latin America. Two out of every five of the reports for this area were from the chemical industry.

<sup>&</sup>lt;sup>50</sup> Theodore R. Gates and Fabian Linden, Costs and Competition: American Experience Abroad, Studies in Business Economics, No. 73, 1961.

					Produ	tion cost			Scale	economies	in produc	tion costs	
	Capa thous	sand	<i>K</i> ₿/ <i>T</i> .		a	nt distrib (%)	ution	1	lot <b>ai</b>			tribution O	•
Product	1 <b>00</b> /	/ <b>37</b> .	•/ * -	Total \$/T.	1			_	1	1		11	m
				-	Cap.	Lab.		₿/T.	et O <sub>4</sub>	Cap.	Lab.	Others	Mat
	(1	)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	an	(12)
Isopropyl	(O <sub>n</sub> )	6	242	92.4	33.3	28.7	38.0	-			_		
Alcohol	-	12	167	71.6	<b>29</b> .6	21.3	49.1	20.8	22.5	10.3	5.5	6.7	
		30	107	56.7	24.0	14.0	62.0	35.8	38.7	18.5	8.8	11.4	-
Polyviny1	(O <sub>a</sub> )	6	285	290.3	13.3	16.3	70.4						
Chloride		20	170	250.4	9.5	8.8	81.7	39.9	13.7	5.1	3.9	4.7	_
(PVC)		40	129	239.1	7.6	6.1	86.3	53.2	18.3	7.0	5.1	6.2	
Butadiene	(O <sub>0</sub> )	10	600	239.4	35.1	18.6	46.3						
		20	450	201.5	31.3	13.6	55.1	38.2	16.0	8.8	3.3	3.9	
	······································	40	337 5	177.5	26.5	11.1	62.4	61.9	25.9	15.5	4.4	6.0	-
Carbon black	(O <sub>9</sub> )	10	300	130.3	35.4	21.0	43.6						
		25	208	104.1	29.0	16.5	54.5	26.2	20.1	12.3	3.2	4.6	_
		50	160	90.3	24.8	12.5	62.7	40.0	30.7	18.3	5.2	7.2	_
Ethylene (gasoline)		10	570	184.7	46.3	21.8	31.9		_	_		_	
		20 60	413	144.8	42.8	17.9	39.3	39.9	21.6	12.7	2.4	5.4	1.1
		<del></del>	250	104.6	35.8	13.9	50.3	80.1	43.4	26.0	3.9	10.1	3.4
Urea		33	85	64.2	18.5	13.3	68.2	_	_	_	_		_
		82 65	63	58.5	15.5	9.8	74.7	5.6	8.8	4.4	2.3	2.1	_
			<b>50</b>	54.3	13.0	6.6	80.5	9.9	15.4	7.6	4.0	3.8	-
Acetylene (natural gas)	•	13.6	465	198.4	32.8	15.2	52.0	_	_	_	_		
		27.2	376	176.3	29.9	11.7	58.4	22.2	11.2	6.4	1.9	2.9	_
		45 	320	165.6	27.0	10.7	62.3	32.8	16.5	10.2	2.3	4.0	—
kyrene		10	280	250.3	15.7	11.6	72.7						
		25 70	224	231.8	13.5	8.0	78.5	18.5	7.4	3.1	2.0	2.3	_
			177	220.9	11.2	6.4	82.4	29.4	11.7	5.8	2.6	3.3	—
olyethylene (high pressure)	•	8.13	492	<b>267</b> .0	26.7	15.3	58.0	_	_				
		12	417	249.6	24.2	13.6	62.2	17.4	6.5	4.1	1.0	1.4	
		24	383	240.4	23.1	12.6	64.3	26.5	9.9	5.9	1.9	2.1	
mmonia (natural gas)	(0,) 3		139	46.4	41.9	23.1	35.0	_					
	10 18		106	37.6	37.9	18.9	43.2	8.2	18.9	11.2	2.6	5.1	
	14	NU I	89	34.2	36.5	16.0	47.5	12.2	26.4	15.1	4.0	7.3	

#### TABLE 10. SCALE ECONOMIES IN PRODUCTION COSTS FOR SELECTED PETROCHEMICALS

Sounce: United Nations/BCLA, Lo Industrie Quimice on Américe Lotins, 1964, annex XVIII, table B. Notes:

3 ų,

II - Labour costs, including supervision and overhead as %, main-tenance and also interests on working capital.
 III - Cost of raw materials and supplie, including additives, esta-lysts, solvents etc.
 (0.) - Reference capacity.

K - Capital investment.
 I - Capital costs, including depreciation, interest of fixed capital and inservance.

Per details on methodology see Source.

Total unit costs were broken down for comparison into the following costs components: material, labour, plant overhead, plant subtotal, selling and distribution and administrative. The main results of the survey were as follows:

#### (a) Materials

Costs in Latin America were reported higher than in the United States in more than 80 per cent of the cases. The United States also had a comparative advantage in the majority of cases vis-à-vis Europe, Canada and other areas.

#### (b) Labour

With the exception of Australia, labour costs were reported to be consistently lower in a majority of cases for all areas. Latin America had lower labour costs in 68 per cent of the cases.

#### (c) Plant overhead

Europe had lower overhead costs than the United States in more than two-thirds of the cases, while Latin American countries had a higher overhead cost in about 60 per cent of the cases reported.

#### (d) Plant subtotal

These costs were lower than in the United States in a majority of cases (about 55 per cent) only in Europe, while Latin American costs were reported to be higher in two-thirds of the cases.

#### (c) Selling and distribution

Selling costs were reported to be lower than in the United States in a majority of cases for all areas; in Latin American countries in 56 per cent of the cases.

#### (f) General and administrative

These costs were again lower only in Europe, while from Latin American cases reported about two-thirds gave higher costs than the United States.

#### (g) Total unit cost

As a result, total unit costs were lower than the United States cost in two-thirds of the cases for European Economic Community (EEC) countries in Europe, and in about three-fourths of all cases in the United Kingdom, while Latin America had lower total unit cost in only 30 per cent of the cases.

The most common reasons given for higher costs than in the United States were based on a smaller volume of operations abroad than in the United States.

With regard to industry differentials which might be of specific interest, the results reported in chemicals and allied products are shown in table 11.

Some conclusions from this study are:

(a) Chemicals was one of the industries where more cases of lower costs than in the United States were reported;<sup>51</sup>

(b) While materials were more costly than in the United States, labour, overhead, and sales costs were comparatively advantageous abroad;

(c) Seven out of the eight chemical industry reports from United Kingdom operations were of "lower" costs; in EEC, five of the eight chemical industry reports represented lower manufacturing costs than in the United States, while in Latin America 10 of the 21 observations of chemical products were of "lower" costs.

#### COMPARATIVE COST AND CAPITAL INVESTED

It has been frequently argued that countries like the United States with relatively higher labour costs will be more competitive in world markets with products of the more capital-intensive industries. To test this proposition the criterion of average amount of capital invested per worker was used.

For products derived from an industry with \$20,000 or more invested per worker, more than 60 per cent of the reports revealed United States cost advantages — a proportion well above that for the total data assembled in the survey. The only industrial sector in this group was

TABLE 11. PERCENTAGE DETRIBUTION OF COSTS COMPARED TO UNITED STATES OF AMARICA TOTAL UNIT COSTS FOR CHEMICALS AND ALLEED INDUSTRIES, BY COST CATEGORY

		Total		Plant			<i></i>	
Tele!		x	Masarial X	Latour X	Overhead X	Sector Manual X	Salar X	X
Costs iower		50	18	58	48	29	72	40
Costs same	•••••••	14 36	12 70	10 32	6 46	8 63	10 18	6 54
	TOTAL	100	100	100	100	100	100	100

Sounce: Coots and Composition, etc., table 8-a.

<sup>&</sup>lt;sup>31</sup> The ranking was: stoms, clay and glass products, with 73 per cent of the cases; instruments and related products, 62 per cent; fabricated metal products, 36 per cent; chemicals, 50 per cent; machinery except electrical, 47 per cent; paper and paper products, 36 per cent; food and kindred products, 33 per cent; transportation equipment, 30 per cent.

chemicals and allied products.<sup>32</sup> In the next lower bracket (\$15,000-\$20,000 invested per worker), the frequency of the cost advantage declined slightly but was still about 60 per cent of all the reported cases. When the last bracket (less than \$15,000) was reached, costs became more evenly balanced and the number of "same" costs and "lower" foreign costs actually exceeded those indicating any United States cost advantage.

Of the major inputs, unil labour costs showed the most direct relationship to capital investment. Although the labour advantage abroad was pervasive, its influence on comparative costs became diluted where relatively larger amounts of capital were involved.

The general effect of a rise in the scale of operations was also summarized from the survey results:

"Products manufactured abroad at lower costs are, on the average, made in plants whose volume is at least half or more than that of the American plant. Products with similar costs here and overseas have an average volume ratio of substantially less, roughly one fifth of home operations; the higher cost products average a still smaller volume ratio, about 15 per cent of domestic activity".<sup>30</sup>

A more recent study was conducted by a consulting firm for the Synthetic Organic Chemical Manufacturers Association (SOCMA), to evaluate the possible effects of changes in the tariff structure on imports of organic chemicals.<sup>34</sup>

To review the competitive position of the United States organic chemical industry, at first a comparison of costs was made among European, Japanese and United States manufacturers for several organic chemicals among them, phthalic anhydride, trichlorethylene, vinyl acetate monomer and polyvinyl chloride. Later on, twelve more chemicals were added, including a number of primary heavy organic chemicals.

The SOCMA study showed that for most products a European or Japanese producer should have a cost advantage over his counterpart in the United States. The major reasons for this advantage being:

(a) Plant investment costs abroad are typically 80 per cent to 95 per cent of the cost of comparable plant built in the United States;

(b) Many raw material prices are equal to, or less than, United States prices;

(c) Labour costs abroad, even adjusting for productivity and fringe benefits are only 30 per cent to 40 per cent of United States costs;

(d) Sales and administrative costs are lower abroad than in the United States.

The only major cost item in which the United States has an advantage is energy. United States' energy costs are generally no more than 60 per cent to 80 per cent of energy charges abroad. There are also cases where United States costs are lower because the product is derived directly from a basic energy source like natural gas.

Manufacturing costs were directly related to the penetration of imports into United States markets. For example, the landed cost of naphthol was only about 80 per cent of that of United States costs, and 41 per cent of the naphthol sold in the United States was imported. The cost of imported trichlorethylene was about 95 per cent of United States costs, and about 15 per cent of the domestic demand was met by imports, and in the case of PVC, costs were about the same and imports were negligible. Also in the case of phthalic anhydride the landed cost was 120 per cent of United States costs and imports were also negligible.<sup>25</sup>

In addition, the SOCMA study also found a trend towards a reduction on plant investment costs abroad:

"We discovered that it is now cheaper to build a chemical plant in Japan or Europe than in the United States and this imbalance will probably continue for some time. Just the opposite was true immediately after World War 11 when the high cost of construction materials and equipment and the low productivity of labor outside the United States made it more expensive. Within the last five years, however, the balance has shifted the other way, in spite of the continued rise in labor costs abroad"."

Summarizing, the findings of the SOCMA study were that if raw materials costs were equal, a European or Japanese producer could expect his manufacturing costs of organic chemicals to be 80-85 per cent of the United States costs. Out of the eighteen key organic chemicals and intermediates studied, unit costs for twelve of them were lower abroad than in the United States.

#### THE COST OF RAW MATERIALS AND ENERGY

In a series of studies by chemical companies the costs of the main inputs for chemical production in different areas were compared. A summary of their findings with regard to the cost of raw materials follows.<sup>27</sup>

The United States has a cost advantage in those chemicals produced from natural gas, L.P.G., ethane or field distillates. Natural gas has been priced there independently of its caloric value relationship to other fuels. This has in turn given a low price structure to refinery gas, and L.P.G.

On the other hand, the United States' raw materials cost advantage for chemicals derived from crude oils and naptha is disappearing. Very important is the trend towards utilization of naphtha as the "universal" petrochemical raw material since practically all petrochemicals can be produced from it (see table 12).

<sup>&</sup>lt;sup>36</sup> Data from Costs and Competition, etc., table 8-c, p. 114. Classification used was: group 11-\$20,000 and over: chemicals and allied products; group 11-\$15,000 to \$20,000: includes food and kindred products, rubber products, paper and paper products, transportation equipment, primary metal products, and instruments and related products; group 111-less than \$15,000: includes stone, clay and glass products, fabricated metal products, machinery except electrical, electrical machinery, miscellaneous products, apparel, and leather products.

<sup>\*</sup> Costs and Competition, etc., p. 128.

<sup>&</sup>lt;sup>14</sup> George B. Hegeman, SOCMA Study, (A. D. Little, 1962).

<sup>&</sup>lt;sup>55</sup> Of course, part of the explanation resides in the present tariff structure, which does not necessarily parallel the prevailing ratios in manufacturing costs.

<sup>\*</sup> SOCMA Study, p. 4.

<sup>&</sup>lt;sup>21</sup> Chemical Engineering Progress, vol. 58, No. 2 (February 1962).

In general, there is good correlation between the cost of the cheapest energy source, and costs of chemicals with high energy content, like ammonia, nethancl, hydrogen cyanide and its derivatives (see table 13). Also, when comparing costs of basic and pure hydrocarbons the following points are apparent:

(a) United States Gulf Coast prices are lower for all basic hydrocarbons than in other countries. The cheapness and availability of natural gas explains this. The general trend is for the difference to become smaller above propane.

(b) In pure hydrocarbons, the United States has clear cut advantage on all but acetylene (table 14).

It is interesting to compare at this point prices for intermediates and other more processed products, to see if this advantage is retained while value is added to the product through successive processing steps. Such data are presented in table 15, for the United States and its main European competitors and it provides further evidence that European costs having been decreasing during the last five years have now reached the point where many petrochemicals sell below United States prices.

#### **PRICING OF EXPORTS**

Export prices for chemical products may be established to reflect not average production cost, but the cost of incremental output.

Petrochemical plants being capital intensive continuousprocess operations, it is possible, by increasing production by only a small amount, to achieve a substantial reduction in unit costs. Thus export sales can become an outlet for lowering over-all unit costs, by operating at a higher rate of capacity utilization. The additional output could be priced at no more than the variable costs, since fixed costs are already covered, this would be the marginal cost of production, and in fact it is widely used as a basis for pricing chemical exports.

TABLE	12.	ENERGY	COSTS	POR	SELECT	Ð	COUNTRIES,	1962
		(In S	cents	per	million	B)	TU)	

	United States (Gulf Coast)		Fod. Rep. of Germany	lialy .	France	Japan
Primary fuels						
Coal	30-35	52-54	50-65	55-70	60-64	57
Crude Oil	45-50	35-45 =	35-45 *	35-45 +	35-45 *	40-50
Natural gas	17-23	ca. 80-100		ca. 60		
Secondary fuels						
LPG	38-50	ca. 100-110	ca. 100-110	ca. 100-110	ca. 100-110	150
Naphtha	50-70	60-70	60-70	60-70	60-70	60-70
Bunker oil	30-35	50-60	45-55	40-50	ca. 65	45-50
Electric power						
Steam	0. <b>7-0.9</b>	1.5	ca. 1.0	ca. 1.5	1.4	1.0
Hydroelectric		c	Beographically	restricted		
			range ca. 0.3			

SOURCE: Chemical Engineering Progress, vol. 58, No. 2 (February 1962), p. 20. \* Ex-Tax.

TABLE 13. COST COMPARISON OF FUEL CHEMICALS WITH ENERGY COSTS FOR BELIEVED COUNTRIES, 1962

	United States (Gulf Count)	United Kingdom	Pol. Rep. of Gormany	italy	Prance	Japan
Champest fuel	1 <b>7-23</b>	<b>50-6</b> 0	35-50	40-50	ca. 65	45-50
Chemiede			Canto par paun	/		
Ammonie			4.1	5.3-5.8	7.2	
Hydrogen cyanide Urea	12 4.3	4.8	os. 17	5.2-5.6	5.9	-

Sounce: Mid., p. 20.

## TABLE 14. COSTS OF BASIC AND PURE HYDROCARBONS FOR SELECTED COUNTRIES, 1962 (Cents per pound)

	United States Guif Coast	United States East Coast	United Kingdom	Fed. Rep. of Germany	indy	France	Jap <del>an</del>
Basic hydrocarbons							
Methane Ethane Propane N-Butane 90 % Propylene Naphthas (light and heavy)	0.75-1.0 0.8-1.1 1.0-1.2 ← ca.		<b>ca</b> . 2.0-2.5	iot sepai (Mix ci	nated (ca ed with ( . 2.0-2.2 3.2-3.5	C <sub>4</sub> 's)	
we hydrocarbons							
Ethylene	4.8-5.0 8.5-10.0 3.5	5.0-6.25 12-15 3.5	¢	- 11-14	l		15
Butadiene	ca. 12 ca. 15	12.75	¢	- 14-16	i ——		15-16.5
Benzene.	4.2	4.2	۹ ۱				

SOURCE: Chemical Engineering Progress, vol. 58, No. 2 (February 1962), p. 21, tables 3 and 4.

TABLE 15. COMPARATIVE PRICES OF SELECTED PETROCHEMICALS, 1963

						United States	United King- dom	France	Pod. Rep. of Germany	itely										
Acetone																6.5	7.4	6.0	6.7	5.1
Detergent alkylate .																10.2	8.0	8.2	8.6	8.0
Isopropanol																7.0	7.9	6.5	6.5	8.0
Methanol, synthetic.	•			•		•										5.3	4.7	4.4	3.9	5.2
Styrene monomer.	•															12.5	11.7	10.9	11.7	10.2
Polyethylene, low der	Mİ	ly	(it	je	cti	ioi	1)	ø	sd	C,	10	-tı	DN	lo	ts.	21.5	22.2	19.4	20.1	22.9
PVC; general purpos	6,	5-1	0	ı l	oti	8.										16.0	15.8	17.6	16.9	14.2
SBR rubber, 1500 gri	Ide	э,	10	to	۵	lo	ts.	•								23.0	23.1	19.6	21.8	22.1

SOURCE: European Chemical News, July 12, 1963.

In the Mexican scheme regulating the development of the petrochemical industries, the pricing of output satisfying domestic demand is based on matching fixed plus variable costs (break-even point for each plant), and local prices can be up to 15 per cent higher than United States prices, provided that raw materials are available at equivalent prices, while additional revenue and profits are to be obtained via exports.<sup>35</sup>

In the SOCMA study, marginal costs (MC) were computed for the chemicals selected, and to these calculated MC the additional costs of importing from Europe and Japan into the United States were added. These included: transportation, insurance, commissions, etc.

The data available for four of these products: formaldehyde, phthalic anhydride, PVC and trichlorethylene, show that lowest landed costs (with marginal cost pricing) were lower than United States costs in three of the four cases: phthalic anhydride, PVC and trichlorethylene. Thus, the protection afforded by the present tariff structure in fact prevented substantial imports.

Other factors affecting chemical trade, besides costs and tariffs, are as examples: arrangements for captive sale, regional preferences, customer loyalties, etc.

The SOCMA study finally forecasted:

"Chemical plant capacity abroad will undoubtedly continue to grow over the next several years; local demand there is already being met; and future growth must be based on expansion into other markets particularly in the United States, the world's largest consumer of organic chemicals ".<sup>39</sup>

<sup>&</sup>lt;sup>20</sup> See chapter V, 15, "The Mexican Government and the Petrochemical Industry in Mexico".

<sup>\*</sup> SOCMA Study, p. 6.

## 8. Petrochemical industrial pattern

# INTERINDUSTRY RELATIONSHIPS

Petrochemical industries are characterized by a high ratio of intermediate to total demand. Table 16 illustrates this for average values of this ratio (w) for a sample of countries. Chemicals and petroleum products are included among the productive sectors characterized to be as of "intermediate manufacture".

Output of these industries is absorbed by the chemical industry itself, rubber products, textiles and agriculture among the main users.<sup>30</sup>

In addition to this statistical evidence there are linkages between agriculture and petrochemical production via nitrogenous fertilizers; between rubber production and plastics via styrene which can be polimerized to polystyrene; between plastics and fibres, etc. Another important connexion is the relationship with the automotive industry via synthetic rubber for tyres, plastics for parts, upholstery, insulation, etc., and also through the so called automotive chemicals: anti-freezers, anti-knock agents, fuel additives, etc.

On account of all these relationships the question which presents itself to the consideration of developing countries planning to establish petrochemical industries is whether it is feasible to install such industries before there exists an industrial infrastructure and level of consumer demand as to permit the balanced growth of

<sup>30</sup> See Hollis B. Chenery and Paul G. Clark, *Interindustry Economics*, National input-output tables for United States, Japan, Italy, Norway.

the industry. The alternative advocated by many is to start step by step, substituting imports of finished products and by working backwards finally integrate production including that of basic intermediates.

# IMPORT SUBSTITUTION AND BACKWARD INTEGRATION

To start industrialization by giving the "last touches" to imported materials might be convenient inasmuch as it starts industries even where markets are small and technical know-how and capital scarce. But, it has also disadvantages. Although it is often taken for granted, in dealing with import substitution through backward integration, that as soon as domestic demands reaches a minimum economic size, domestic production will be started, some forces tend to counteract this trend.

The domestic producer who has been using hitherto imported materials will many times be hostile to the establishment of local industries producing these materials. He may have fears about the low quality of local production that he may become dependent on only one source of supply, and that competition may increase once the basic raw materials are produced domestically.<sup>21</sup>

In addition, there is also the danger that once this gradual process of backward integration is started, it becomes increasingly difficult to stop imports of raw materials and other required inputs because of a whole array of economic and social implications. This may

<sup>31</sup> It is a well-known fact that the interests of the finishing, assembling, converting and mixing industries in developing countries have very often been opposed to the establishment of domestic sources of supply for their basic imports.

		PINAL (LOW W)			INTERMEDIATE (High w)								
		Pinal manufacture	w		"	Intermodiate manufacture	*						
	3	Apparel	0.12	0.69	13	Iron and steel.	0.78						
	4	Shipbuilding	0.14	0.58	22	Paper and products	0.78	0.66					
		Leather and products	0.37	0.66	28	Petroleum products		0.57					
	1	Processed foods	0.15	0.61	19	Nonferrous metals.	0.68 0.81	0.65					
Manufacture	2	Grain mill products	0.42	0.89	16	Chemicale	0.69	0.61					
Manufactor of	••• • •	Transport equipment	0.20	0.60	23	Coal products.	0.67	0.60					
	7	Machinery	0.28	0.51	11	Rubber products	0.48	0.63					
	15	Lumber and wood products.	0.38	0.61	12	Textiles	0.57	0.51					
	14	Nonmetallic mineral products.	0.30	0.47	- 9	Printing and publishing	0.37	0.69					
	10	Industry n.s.c.	0.20	0.43	•		0.40	0.49					
	17	Pinal primary production			1	Intermediate primary production							
	14	Commodities			17	Agriculture and forestry	0.72	0.31					
		6 fishing	0.36	0.24	27	Coal mining	0.87	0.23					
Primary production	) B	Services			20	Motal mining .	0.93	0.21					
	· • }	25 Transport	0.26	0.31	29	Petroleum and astural gas	0.97	0.15					
		21 trade	0.17	0.16	18	Nonmetallic minerals	0.52	0.17					
	ŗ	26 aervices	0.34	0.19	24	Electric power	0.59	0.27					

TABLE 16. CLASSIFICATION OF PRODUCTIVE SECTORS ACCORDING TO RATIO OF INTERMEDIATE TO TOTAL PRODUCTION \*

Bounce: Hollis B. Channy and Paul G. Clark, p. 207. Interindustry Economics. \* The sectors are numbered is order of triangularity. The values of w are averages for Italy, Japan and the United States, w - ratio of intermodiate to total domand. impose excessive strain on the balance of payments and build in the long run a trend for a structural deficit.

If, in addition, the industry is entirely based on converting imported materials, these imports of semi-finished materials, always ready to rush in from abroad whenever an industrial project is being considered, are real "leakages" of development effects.

"Therefore, excessive gradualism in introducing industry by successive small bits of value added may not pay off. Whereas the first steps are easy to take by themselves, they can make it difficult to take the next ones "...

"Certainly, but for the process of starting with the 'last touches' many industries could never be undertaken at all in under-developed countries; once this is recognized, however, much is to be said for 'biting off as large pieces of value added at a time' as the country can possible digest."<sup>28</sup>

#### CONCLUSIONS

Developing countries have in recent years paid considerable attention to the development of petrochemical industries and most of them plan to continue stressing investment in this strategic sector of industry.

An examination was made of different economic aspects which are characteristic of the petrochemical industry: its interconnexion with other industrial branches, raw materials, capital, labour and know-how, requirements; as well as various institutional conditions determinant in its development. The following tentative conclusions emerge from our analysis:

(a) Petrochemical industries were developed, and are being installed at first in developing countries having large enough markets as to absorb domestically most of their output. In this category fall such countries as: India, Brazil, Mexico, Argentina.

(b) In other countries where domestic demand is much more limited because of smaller population and income like: Trinidad, Iran, Algiers, petrochemical plants are being projected and/or being constructed with an eye on export markets in addition to the substitution of imports. The development in such cases is stongly based on the availability of ample surplus of raw materials like natural gas and oil.

(c) There are definite economies of scale in the production of most petrochemical products, especially those of a more basic and intermediate nature. In addition, capital requirements are very high, and those for unskilled labour very low. While the capital investment required for a minimum economic size plan( of most basic intermediates is very high and the output implied exceeds by far local demand in the majority of developing countries, development of many of the end-products requires sophisticated technology and operating knowhow, as well as a structure of industrial and consumer demand which are only to be found in the most industrialized countries. This poses a dilemma to developing countries who do not seem to meet the pre-conditions for economic production in either case, caught in a squeeze between huge capital investment and plantsize sophisticated technologial requirements.

(d) The petrochemical industry is by no means an homogenous industrial sector, and many of the abovementioned are generalizations which break down when a more detailed analysis (at the product level) is carried through. Also, the structure of demand for these products cannot be patterned for many developing countries along the same lines of development followed in either the United States or Europe. For example, in the United States, one of the biggest markets for petrochemical products is the huge automotive industry. Its demand for anti-knock agents like lead-tetrathyl, anti-freezers like ethylene-glycol, synthetic rubber for tyres, plastics and synthetic fibres for body-parts and upholstery, are not likely to be matched even in the near future in most developing countries owing to a quite different set of conditions ranging from climate to economic infrastructure and income distribution.

(e) On the other hand, the development of petrochemical production in many countries is being oriented towards fulfilling the requirement of given local conditions such as utilizing a particular endowment with natural resources, increasing the productivity of agricultural production, and certain targets of industrial development. An analysis of existing or projected petrochemical plants in developing countries such as was done in section 3. clearly indicates the existence of a hierarchy or sequence being followed in the development of petrochemical production in developing countries. A majority of the plants are ammonia-producing plants, this being converted into urea and other nitrogenous fertilizers in order to spur agricultural productivity and meet a growing demand for food. Also, there is a close connexion between the relative level of industrial development and the establishment of petrochemical plants, as indicated by the concentration of plants in the relatively more industrially advanced of the developing areas: Latin America and the Far East and in these areas being mostly concentrated in a few of the larger and more developed countries. At the same time, plants producing petrochemical products requiring much more advanced and less divulgated technology, and/or implying a more sophisticated structure of consumer demand, like plastics, synthetic rubber, synthetic fibres and detergents, are very few and they are scattered among a small number of countries such as those mentioned before.

(*j*) Nevertheless, a trend is distinguishable in the direction of increasing and more diversified petrochemical production to be originated in developing countries in coming years. There are several factors at work favouring such a development, *inter alia*:

- The increased awareness about the strategic role that this industry may play in inducing further economic growth;
- The discovery and exploitation in some countries of untapped oil and natural gas deposits, coupled with a recent trend towards setting up market based refineries in others;

<sup>&</sup>lt;sup>20</sup> Albert O. Hirschman, The Strategy of Economic Development (Yale University Press, 1962), pp. 118-119.

- The formation of regional trade groupings which tend to stimulate the establishment of new, large-scale plants to supply an enlarged market;
- The change taking place in institutional international arrangements favouring the transfer of technology and funds, through a more competitive division of labour among the chemical and vil companies, and the financial, engineering and contracting agents of the industrialized countries;
- A trend towards ascribing to national oil state agencies at least some of the work to be done in the development of petrochemical production in developing

countries. This has the following advantages: control of the supply of raw materials, either natural gas or refinery feed-stocks, utilization of existing cadres of professionals, technicians and skilled labour, utilization of an existing organizational framework and distribution system, financial resources and company size which enable easy access to international financing and know-how acquisition, etc. Some successful examples are: PEMEX in Mexico and PETROBAS in Brazil, and similar policies are being pursued by YPF of Argentina, YPFB of Bolivia and oil state agencies in several other countries.

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# 2. THE PETROCHEMICAL INDUSTRIES General information

Propared for the United Nations Centre for Industrial Development by l'Institut français du pourele

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#### Introduction

Between the two world wars the petrochemical industry grew slowly to meet the needs of the automobile industry by supplying it with such products as new types of paint, antifreeze and additives. Then, towards the end of this period, synthetic rubber and plastics made their appearance. Lastly, the Second World War acted as a powerful stimulus on the development of chemical synthesis products put out by this new industry to meet a demand which surpassed the possibilities of such conventional sources as the coal industry and farm production, whether it was a question of quantities needed or the quality required.

The petrochemical industry is distinguished by its dynamism and rapidity of development. Its dynamism lies in the demand it has to face and its rapid development concerns techniques as well as far-reaching and rapid changes in its industrial structures and implantations.

#### NEW MATERIALS

The utilization of oil and gas as sources for the production of chemical products was made possible by the development of molecular structure transformation techniques which led to a production increase of certain products and enabled new types of artificial materials to be manufactured while the conventional chemical industry was not able to satisfy the needs of the market by showing itself incapable of producing new materials.

The utilization of these materials was developing along with these techniques. Detergents, synthetic fibres and plastics, all of which are manufactured from chemical synthesis materials, created new markets which expanded very rapidly. The same was true of other products such as fertilizers and synthetic rubber which now have a very large turnover.

#### LARGE-SCALE AVAILABILITY AND CHRITAINTY OF SUPPLY

The existence of enormous resources of crude oil or natural gas and the highly competitive and stable prices at which petroleum cuts can be offered as raw materials, along with the certainty and regularity of the supply, are additional causes in the increased demand for petroleum products.

The abundance of the available supply has had a considerable effect on the domand. The existence, in larger and larger quantities, of light distillates, networkly gas and refinery gas, mainly due to the development of refining, has meant that new outlets have had to be found which, in turn, has stimulated the search for new uses.

Other sources of raw materials, such as molacess for ethyl alcohol and coal tar for beamas, required either a certain amount of time or else the magufacturing of cohe, and in both cases prices tended to be unreliable.

#### EXPANSION OF DESITING HARAFTS AND CREATION OF NEW FINISHING PRODUCTS

The general rise in the standard of living and, consequently, the increase in concumption per inhabitant as well as the creation of new outlets have had the following result:

- Intensification in the search for new applications for the products. This can be seen in the invasion of synthetic materials on markets which were formerly dominated by traditional products.
  - Synthetic fibres have made their way into the textile industry to the detriment of cotton and wool.
  - In the rubbe- industry the most recent synthetic products have qualities which are equal and sometimes superior to those of natural rubber. These synthetic products are more stable from the point of view of price, and their output is not dependent on political events.
  - In the field of packing, polyethylene has widely replaced glass and cellophane. Plastics have also made their way into the field of construction where their resistance to corrosion and inclemency, their lightness and their flexibility are precious assets.
- The possibility of putting finished products on the market at attractive prices by improving production costs through the discovery of new processes or methods by technological advances in existing processes, and by technical improvements in instrument and equipment design.
- The orientation of research towards the diversification of processes so that chemical products can be produced from several raw materials.

Under the impetus of lively commercial competition, the petrochemical industry is a difficult field, but the dynamism of its expansion justifies the attempt to develop it in countries which have:

Large reserves of raw materials such as oil and natural gas;

- Existing consumer markets which are sufficiently develeged or which are destined to expand considerably to support the creation of such an indu: try;
- Favourable export conditions even despite the competition imposed by the international market.

# Part I. Description and speedle characteristics of the petrochemical industry

## 1.1 DESCRIPTION OF THE INDUSTRY AT THE PRESENT MOMENT

#### I.I.I. RAW MATERIALS

The reasons behind the utilization of larger and larger quantities of all and natural gas as raw materials in the shoules industry are as follows:

(1) Oli and natural gas can produce purer products than those from carbochemical origin.

(2) Potroloum refining can, by means of normal or special processing, produce substances which it is difficult to derive from other sources (xylenes).

(3) Oil and natural gas one increase supplies of certain products which would not otherwise be available in sufficient quantities (glycosin). (4) Oil and natural gas can usually produce the required products at lower prices than can other sources (plastics).

Raw materials come from sources which are sried and adapted to local conditions. They are made up either of primary hydrocarbons simply separated from natural gas or oil, or of products which have already been transformed such as residual gas or petroleum cuts left over from refining. Large amounts of chlorine are also consumed.

In the United States use is mainly made of natural gas as well as ethane and the liquefied gas extracted from it. Gas from catalytic cracking, which is rich in olefins, is also an interesting source. Aromatics are extracted from reformed gasoline.

Europe, which has only recently been able to exploit its own natural gas resources and which, as a result of the structure of the petroleum market, is less heavily equipped with catalytic cracking plants, has centred its petrochemical industry around excess light gasoline which is difficult to valorize on the European market where large quantities of medium distillates are consumed.

Primary hydrocarbons continue to be a favourable source for industries, even though the current disfavour towards acetylene eliminates an important outlet for natural gas. Some industries which consume large quantities of gas, as is the case for ammonia, have installed themselves near production fields, far from any market. For example, ammonia plants have been built :

- In the Caribbean, on Trinidad, where Federation Chemicals Ltd., an affiliate of W. R. Grace & Co., has just begun production at its 235,000 T/year plant, thus increasing the total output to 500,000 T/year if existing installations are also added on.
- In the West Indies, on Aruba, where Antilles Chemical & Co., an affiliate of Standard Oil of New Jersey, has built a 360 T/day ammonia plant to supply its urea and nitrate installations and to export to Latin America.

In addition, naphtha is widely used in countries which do not have primary hydrocarbons at their disposal. A European petrochemical industry based on naphtha is being established. The same is true in India where the excess naphtha produced by refineries is used as a raw material in the production of ammonia and fertilizer and in the production of olefins by steam cracking. This trend is accelerated by the fact that naphtha processes are undergoing numerous improvements.

#### I.I.2. LOCATION

The larger' centres can usually be found in regions where crude oil refining and natural gas availability are most highly developed. This is the case in Texas and Louisians in the United States. This is also the case of the leading petrochemical implantations in Europe :

The S.N.P.A. and the Pardies Complex near the natural gas deposit at Lacq, France.

The ENI and the Ravenna Complex in Italy.

Naphthachimie and the Sholi Potrochemical Units near the Borro Lake refineries in France. The Esso Standard and C F.R. petrochemical productions near the Basse-Seine refineries in France.

The Shell petrochemical productions in Rotterdam, the Netherlands.

This dense concentration of similar types of activity can be seen immediately upon the creation of s new complex. It enables the initial efforts to be better valorized while making the most of the multiplication effect it entails by reducing investment burdens necessitated by associated services and the production of utilities and by decreasing production costs by providing for more widespread utilization of by-products.

I.1.3. PRODUCERS AND THE BELATIVE POSITION OF PETRO-LEUM AND CHEMICAL PRODUCTS COMPANIES INTERBITED IN THE PETROCHEMICAL INDUSTRY

As a general rule, the former supply the latter with raw materials, and the latter manufacture finished products.

However, there are many exceptions to this rule, and the integration of petroleum and chemical activities is carried to greater or lesser degrees, depending on the case. The same company can also be engaged in several activities.

(1) Some oil companies supply the chemical industry with raw materials and intermediate products. These are: Standard Oil of New Jersey, S. O. of California, Shell, Gulf in the United States; Shell, Compagnie de Raffinage, Esso-Standard, S.N.P.A. in France; British Petroleum Co., Shell Chemical, Esso Petroleum Co. in the United Kingdom: and the ENI in Italy.

(2) Some chemical companies depend on the oil industry for large quantities of raw materiala and intermediates. They devote most of their efforts to manufacturing complex products and are specialized in organic chemistry products. These are: Du Pont, Monsantc, Rohm& Haas, Wyandotte in the United States; Pechiney, Saint-Gobain, Rhône-Poulenc, Progil, Ugine & Kuhiman in France; Monsanto Chemicals Ltd., in the United Kingdom; Bayer, Hoschet & BASF in Germany (Fed. Rep.); and Sicedison in Italy.

(3) Other oil companies extend their activities beyond basic products to include intermediate products and their derivatives and even to end-products : Shell in the United Kingdom, the United States and France; Antar in France; and the ENI in Italy.

(4) There are also some companies which do not make large-scale domands of raw materials and which usually make use of natural gas, liquefied petroleum gas, refinery gas and maphths: Imperial Chemicals Industries in the United Kingdom; Naphthachimis in France; and Montecatini & Edison in Italy.

(5) Some chemical companies team up with oil companies to carry out joint activities. There are many arrangements of this sort in Europe, for example: British Petroleum Co. (50 per cent) and National Distillers (50 per cent) in the United Kingdom; and Naphthachimie (BP and Pechinoy) and Shell-Saint-Gobain in Pranse. (6) Chemical companies also have a tendency to buy up plastic manufacturing plants and the like. In this manner they guarantee themselves an outlet for some of their products at the same time as acquiring technological and practical experience in the field in question. This is the case with Imperial Chemical Industries which is the largest producer of polyethylene films in the United Kingdom.

(7) Lastly, some companies, in France in particular, pool their resources in order to create affiliates. In this category are Pechiney-Saint-Gobain, Ugine-Progil and Rhône Poulenc-Usines de Melle. These associations sometimes go so far as to include a foreign partner: Progil-Bayer-Ugine, and Kuhlman-Du Pont de Nemours. The main advantages of such associations lie in the following points:

- Possibility of building a large-capacity unit which is competitive on the international market and of avoiding harmful competition between small producers on the domestic market;
- Reduction of investments for each of the companies, thus enabling them to become involved in new fields of activity at the same time,

Certainty of supplies and, reciprocally, of outlets.

It is difficult to evaluate the respective share of production as a whole that is taken up by the different types of structures. But it is quite evident that there is a greater and greater tendency towards integration. This does not, however, often assume the form of vertical integration within the same legal entity, but rather of an association which enables basic product suppliers to cousolidate their outlets and to participate in the profits all along the line right up to the finished products, and it also provides consumer distribution networks with an insurance against fluctuations in the supply of raw materials (certainty and cost) by pooling their production.

The extremely severe competition which exists between the different finished products on the market and the rapid growth of production have led research to be oriented so as to assure the production of chemical products from several basic products or to reduce the intermediary stages to a minimum. This requires, on the part of the numerous interests involved, a pooling of knowledge and a concentration of experience such as has reached an extremely advanced stage in the United Kingdom. An example of this is where refineries, chemical industrial installations and finished product transformation industries are associated and linked together in a comprehensive complex within which they mutually aid each other.

#### 1.2. SPECIFIC CHARACTERISTICS OF THE PETROCHEMICAL INDUSTRY

#### I.2.1. PRINCIPAL PRATURES

#### I.2.1.A. Investment volume

The investments put into petrochemistry are very extensive. This is illustrated by the figures for the four leading European producing countries.

#### INVESTMENTS MADE BY EUROPEAN COUNTRIES FOR PETROCHEMICAL PRODUCTION

(In millions of US dollars)

	1959	1960-62	Total
France	52	248	300
Federal Republic of Germany	80	142	222
Italy	54	238	292
United Kingdom	82	206	288
	268	834	1,102

The size of the sums committed comes partly from the fact that investments are very high per unit. The investment per new job created of approximately \$20,000 to \$100,000 is among the highest in the world.

Furthermore, the position occupied by petrochemical production within the chemical industry becomes larger and larger. In the United States the part taken up by petrochemical products was negligible in 1930. It will have reached 40 per cent of the over-all chemical output in 1965. In the United Kingdom production went from 6 per cent in 1959 to 65 per cent of the organic chemistry industry in 1962. Comparable trends are being experienced in Italy, France, Germany (Fed. Rep.) and Japan. Petrochemical products now account for 57 per cent of the dollar value of all the chemical products in the United States.

This increase in investments does not go on without jolts and sometimes even sets off overcapacity crises which affect all branches of petrochemistry. Butadiene and ethylene in the United States and benzene in Europe have all gone through or are going through such crises. They reveal themselves by a sharp drop in prices and by attempts at dumping. Some upheavals can even lead to the buying up of entire plants by more stable colleagues (buying up of Texas Butadiene by Sinclair and of various Montecatini plants by Shell).

#### Increase in capital cost along with manufacturing of more highly elaborated products

Basic products and intermediates require larger and larger investments as the, progress from the stage of transformation to the state of finished products and then to consumer goods.

(1) The example of the production of ammonia and fertilizers:

For a plant, built in Europe, using natural gas and consisting of:

The production of synthesis gas from natural and supplying 300 T/day of ammonia synthesis;

An output of 300 T/day of ammonia;

A 300 T/day ammonium nitrate (27.5 per cent nitrogen) unit;

A 200 T/day urea unit;

A 212 T/day sulfuric acid unit and a 280 T/day ammonium sulfate unit;

and operating according to the flow sheet below (cf. figure I).

The breakdown of investments is shown in table 1.

TABLE 1. INVESTMENTS \* FOR AMMONIA AND PERTILIZERS PRODUCTION

	Total d	in US Ioliare	Percenta <sub>li</sub> a of total
Basic product :			
Synthesis gas.		3.8	13.1
Intermediary products :			
Ammonia	7.7 2.0		
TOTAL Finished products :		9.7	33.5
Nitric acid and ammonium nitrate Urea Ammonium sulfate.	10.0 4.6 0.8		
Total		15.4	53.4
TOTAL INVESTMENTS		28.9	100.0

\* The following are included in the investment total :

(1) Manufacturing units, royalties and initial expenses for catalyst

(2) The general installations, including: cost of land and its development, production of utilities, major communications, storage and drying of fertilizers, extras and buildings, roads, etc.

(3) Storage of spare parts, interest rates during construction and start-up expenses.

(4) Engineering : studies, construction supervision, purchases, etc.

It can be seen that the production of fertilizers (finished products) requires investments which are 4 times as large as those needed for the production of synthesis gas (basic products) and 1.6 times greater than for the production of ammonia and sulfuric acid (intermediate products).

(2) The example of the production of aromatics, synthetic fibres and plasticizers:

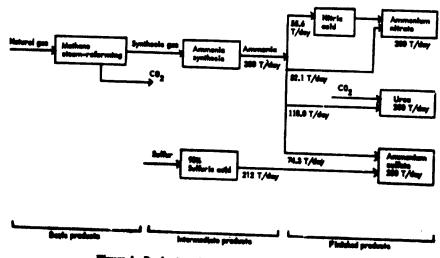
For a plant built in Europe, using a gasoline cut from a refinery, and consisting of:

- A 1st phase of aromatics manufacturing and extraction units producing:
  - 22,500 T/year of benzene (raw material for the production of nylon);
  - 10,500 T/year of O.xylene (raw material for the production of phthalic anhydride-base plasticizers);
- 6,000 T/year of P.xylene (raw material for the production of polyester fibres).
- A 2nd phase of manufacturing units which will lead to the production of:
  - 10,000 T/year of caprolactam which, after polymarization and spinning, will be used to manufacture 9,000 T/year of nylon 6;
  - 7,800 T/year of dimetyl-terephthalate which, after polymerization and spinning, will be used to manufacture 7,800 T/year of polyester fib:es of the "dacron" type;
- 10,000 T/year of phthalic anhydride which will be used to manufacture 10,000 T/year of plasticizers (dioctyl-phthalate) in addition to making available 5,000 T/year of phthalic anhydride which will be used for manufacturing resins and in the polyester industry.
- A 3rd phase of finished products transformation units consisting of:
  - The caprolactam polymerization and spinning units to produce 9,000 T/year of nylon 6;
  - The dimethyl-terephthalate (D.M.T.) polymerization and spinning units to produce 7,800 T/year of polyester fibres;

The production unit for 10,000 T/year of plasticizers;

and operating according to the flow sheet below (figure 2), with the investment breakdown being given in table 2.

It can be seen that the transformation of finished products (3rd manufacturing phase) required investments which are:



. Production of anomania and nitragen fortillaar

- 2 to 3 time higher than for the production of intermediate products and their transformation into finished products (2nd manufacturing phase);
- 5 times higher than the production of basic products (1st manufacturing phase).

TABLE 2. PRODUCING AROMATICS, SYNTHETIC FIBRES AND PLASTICIZERS INVERIMENTS A

Phase	Products	Total ( in millions of US dollars)	Percentage of total
181	Besic products :		
	Aromatics (benzene and xylene).	10.4	13
2nd	Intermediate and finished products :		
	Caprolactam Dimethyl-terephthalate Phthalic anhydride	20	25
3rd	Transformation of finished products	:	
	Nylon 6 Polyester fibres Plasticizers (D.O.P.)	50 Þ	62
	TOTAL INVESTMENTS	80.4	100

Same note as for table 1 concerning all of the supplies included in this total.

• The investment for this 3rd phase is extremely difficult to estimate, because it can vary enormously depending on the characteristics of the nylon 6 filaments wished and the specifications set by the different

#### I.2.1.B. Small amount of raw materials used for some products

Despite extensive sources of crude oil and the highly competitive prices at which the necessary fractions can be offered in the form of raw materials, petrochemical products only represent 2 per cent of the world refinery output, and many sources of potential raw materials (natural gas and gas combined with crude oil) are not

exploited even though large quantities of them are available at low prices. Indeed, the market is not sufficiently developed in some producing countries, and the investments which would be required by the installations needed for on-site recovery, transportation and shipping would be much too large to be covered merely by producing petrochemicals without also planning for other possible utilizations such as for producing energy or for liquefaction.

(1) Consumption of natural gas in a fertilizer producing complex.

For an ammonia and fertilizer production plant made up of units like those described in the flow sheet (I.2.1.A) the consumption of natural gas breaks down as follows:

	gas (chemical consump-	
1ion)		7,700 mª/hr
Fuel for the furnaces and	electric energy production	
by gas turbines		13,400 m³/hr *

\* including 10,100  $m^{*}/hr$  for the production of ammonia.

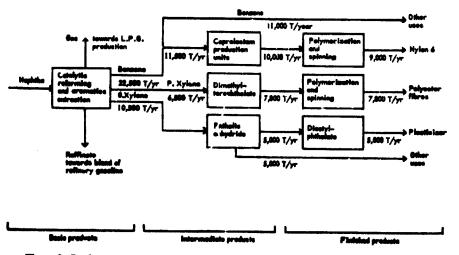
making a total of 21,100 m<sup>3</sup>/hr of natural gas, which represents about:

- 5 per cent of the gas output connected with crude oil in Kuwait:
- 10 per cent of the installed natural gas production capacity in Hassi-Er-R'Mel;
- 2.5 per cent of the current output of the Lacq deposit.

(2) Consumption of naphtha in a steam cracking unit for the production of olefins, diolefins or their derivatives.

The steam cracking of 250,000 T/year of naphtha (i.e., 2.5 per cent of the capacity of a 10,000,000 T/year refinery) can produce intermediate and finished products as shown in the flow sheet in figure 3 and leads to the production of:

33,000 T/year of polyethylene, which is equivalent to India's consumption for 1965-66 or to the expected market in Argentina in 1970.



1

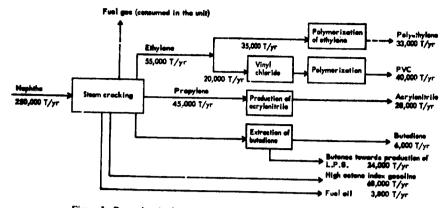


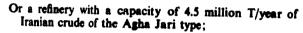
Figure 3. Petrochemical complex based on a steam cracking of naphtha

40,000 T/year of polyvinyl chloride, which is equivalent to the market in India in 1965-66 or to the expected consumption of Brazil in 1970.

Very large refining capacities needed for other products

For example, a benzene output corresponding to flow sheet 2 (I.2.1.A) requires:

Either a refinery with a capacity of 2 million T/year of Sahara crude of the Hassi-Messaoud type;



Or a refinery with a capacity of 7.5 million T/year of Arabian crude of the Ras Tanura type;

Or a refinery with a capacity of 10 million T/year of Iraqi crude.

The required refining capacity increases with crudes which are less rich in aromatics and in aromatic inducing products.

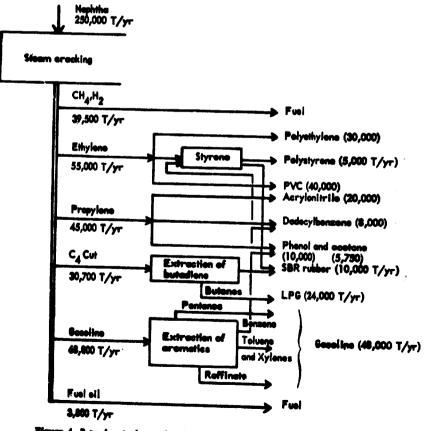


Figure 4. Petrochamical complex beginning from a analytic storm concluses with

# I.2.1.C. Complexity of installations

Based on raw materials which are often made up of several hydrocarbons, proceeding by way of reactions which are not always selective, especially with regard to the production of large intermediates (olefins, for example), petrochemistry frequently leads to the simultaneous production of several products. The result of this is, that in addition to the main product sought after, by-products are obtained which need to be valorized just as much as the main product does if advantage is to be taken of the maximum profitability of the installation. This factor leads to the implantation not of isolated manufactures, but of integrated complexes.

Example: The production of ethylene by steam cracking and the influence of the valorization of the by-products.

Figure 4 shows the succession of operations required in manufacturing: plastics (polyethylene, polystyrene and polyvinyl chloride), detergents (sulfonated dodecylbenzene), synthetic fibres (acrylonitrile), synthetic rubber (styrene-butadiene rubber), phenolic resins and solvents (acetone) as well as the list and tonnage of the products obtained from 250,000 T/year of naphtha.

#### Economic requirements

(1) The finished products market.

If this market cannot absorb such an output, the size of the units must be reduced or the manufacturing of certain products must be eliminated. (2) The minimum economic capacity of the different units.

(3) The valorization of by-products.

(4) When inter-action manufacturing companies are established, it is important that the prices of various by-products also be taken into account.

influence of the cracking capacity and of the valorization of by-products, on the general economy of the operation

Table 3 shows the results corresponding to the following cases :

Case 1. The by-products of ethylene manufacturing, with the exception of butadiene, are not valorized.

Case 2. Propylene is 50 per cent valorized and gasoline can find a suitable outlet.

Case 3. Propylene is 100 per cent valorized and all of the gasoline is sold.

### Results

(1) If the by-products are neither valorized nor used as fuel, ethylene and butadiene are obtained at the respective costs of \$134 per ton and \$250 per ton, which is 20 per cent above the international cost (case 1).

The steam cracking capacity must be approximately 700,000 T/year for ethylene to be produced at the international cost or else the units operate at cost price without any foresceable profit.

TABLE 3. INFLUENCE OF THE VALORIZATION OF STEAM CRACKING BY-PRODUCTS ON THE PRICE OF THE MAIN PRODUCTS : ETHYLENE AND BUTADHENE

	Sale	s price * of pr	nducts and by-	products in \$ U	S/sen
	Ethylene	Dutadiene	Progylene	Intenes	NOR CI-90 Gaseline
Case 1 :					
By-products valorized at their calorific value	134	290		10º Koal Ic value)	18
Case 2 :			<b>、</b>	,	
50 % of the propylene produced is valor- ized, and the gasoline can find a suitable outlet	108	240	70	Calorific	28
Chas 3 ;				value	
Propylene is valorized in its entirety as is					
	100	220	56	Calorific value	28
International price.	100	220	56		28

Notes :

(1) The profits corresponding to a rate of return on investment of 20 % of the total cost of the instalinteger, i.e., a payout time of 5 years, are included in the sales price as well as the taxes which are estimated at 50 % of the profits.

(2) The prices of ethylene and the by-products were set at the pro rate of the international prices. \* The sales price was calculated on the following bases :

Balas all manhaba											-	-						
Price of naphtha	٠																	£15/6nn
الم اشتاق الم معادا								-	-	-	•		•		•	•	•	
Price of fael oil	٠	٠	٠	٠	٠	٠												23.49/10 <sup>0</sup> Keni
Amortiantica																		
ABOTRESSIE	•	•	•	٠	٠	•	٠	•	٠	•	٠	٠	٠	٠	٠	٠	•	
Pinencial charges																		A & V al the boundary
Malatanaa	•	•	•	•		•	•	•	•	•	•	•	•	•	•	•	٠	
MELINGERADOS	٠																	A Y of the immediate
						-	•		•	-	•	•	•	•	•		•	

(2) Partial valorization of by-products shows that a considerable improvement can be made on the cost of ethylene and butadiene (case 2).

(3) Complete valorization gives the whole an excellent profitability and a payout time of 5 years (case 3).

This valorization is only possible if the units producing intermediates from cracking by-products are themselves sufficiently large so as not to lead to intermediates and then to finished products whose cost price is prohibitive. (Cf. "The theory of minimum economic capacity", chapter I.2.1.E).

#### I.2.1.D. Theory of a complex associated with the integration of units so as to better valorize the whole

This also holds true for other economic complexes which engage in various operations but which are characterized by the same general type of production (naphtha cracking to produce acetylene, or catalytic reforming for the production of aromatics). There even appear to be some cases when it whould be best if this integration were carried out to a maximum degree and if the petrochemical complex were built in the neighbourhood of a refinery.

- High octane number gasoline, by-product of ethylene in naphtha steam cracking, should be included in the gasoline pool of a refinery for optimum utilization of its properties.
- Cuts destined for the production of aromatics (benzene and xylenes) are not available and can only be prepared in a refinery.
  - Possibility of utilizing the fractionation columns and catalytic reforming.
  - Optimum valorization of the by-products, such as toluene, metaxylene or ethylbenzene and raffinate, produced in aromatics extraction units, and using them in the soline blend.

#### I.2.I.E. Minimum economic size

This theory is based on the fact that investments do not vary in proportion to the capacity, but rather, according to a power factor generally lying between 0.60 and 0.85. This is the reason why it is advantageous to build large capacity units which cost proportionally less than small or medium capacity units. The same observation can be made for the manpower, general and plant overhead, all of which are proportionally lower expenditures in large capacity units.

The above paragraph (on the production of ethylene) and the following example contain illustrations of this fact :

#### PRODUCTION OF AMMONIA

Capacity . Variable charges * (not including labour)	300 T/day	400 T/day
in US \$/T of ammonia Fixed charges (including labour) in \$/T	9.8	9.8
of ammonia Production cost * in \$/T of ammonia	44.8 54.6	40.2 50

Directly proportional to the or of th

it is n the size of the

ag profits and pro-

#### I.2.1.F. Technical complexity and competition

#### (a) Small, highly qualified manpower

Extremely complex installations make use of the most modern technical developments, especially in such fields as metallurgy, mechanics and control. The staffs operating and maintaining these units must, therefore, make up a highly specialized manpower which has extensive experience. Personnel training problems (engineers, foremen, operators and chemists) are thus extremely important, and the ensuing training expenses are high.

Estimating the work force and personnel qualifications for various types of installations producing : basic products and intermediates

1. Naphtha steam cracking unit for the production of ethylene (55,000 T/year) and propylene (45,000 T/year).

Engineers																	2	per	day
Foremen.																	2	per	day
Chief opera	itoi	Γ.				•											1	per	shift =
<b>Operators</b>																			
Instrument																			
Mechanics	anc	1 a	ssi	sta	เกโ	n	юс	h	an	ics	۱.						2	per	day
									7	Го	TA	L	PE	R	D/	١Y	35	-	

2. Unit for the production of butadiene (40,000 T/year) by the dehydrogenation of n-butane.

Engineers		2 per day
Foreman		
Chief operators		2 per shift
Operators		9 per shift
Instrument maintenance and	control	2 per day
Mechanics		
	TOTAL PER DAY	54

Dependence of the quantity and qualifications of the manpower on the nature and complexity of units

1. Butadiene polymerization unit of 25,000 T/year (not including the pilot plant and the application laboratory).

										То	TA	L.	PE	R	D/	NY.	81		
Maintenance	٠	•	•	·	•	•	·	·	·	·	•	·	·	٠	·	·		per	day
Workers	·	·	·	•	٠	·	·	٠	٠	·	·	·	·	·	·	·	10	per	day
Assistant che	m	lst:	5	٠	•	·	·	·	·	·	·	•	٠	•	•	•	10	per	day
Chemists	·		•	·	٠	٠	·	·	·	·	·	·	٠	•		•	- 4	per	day
Operators .	·	•	·	•	·	·	·	٠			•	•	•				3	per	shift
Chief operat	ог	۱.	•	•	•		•	•		•							2		shift
Foreman	•	•	•		•													per	shift
Technicians		٠	•	•		•	•										6	per	day
Engineers .																	4	per	day

2. Acrylonitrile polymerization and spinning unit (10,000 T/year) (not including application laboratories)

											· · ·					
Engineers		• •			•	•	•									5 per day
Foremen .															1	1 per day 2 per shift
							•	·	·	•	•	•	•	•	l	2 per shift
Chief oper	ato	r a	nd	0	pe	nt	<b>)/18</b>	•	•	•	·	•		•		30 per ahift
ANGICANUS	٠	• •	·	•	•	• •	•	•	•	•	•	•	•	•		15 per shift
Mechanice.	, m	aint	ion	80	80	8.0	d i	ins	tn		en	ts.				15 per day
Chemista .		• •	٠	٠	•	• •	•	•	•	•		•	•			2 per day
Assistant o	her	nist	8	·	·	•	•	•	•	•	·	•	•	•	•	2 per shift
								1	<b>r</b> ~	-		_				210

TOTAL PER DAY 219

id on 4 shifts per day to allow for leave and absence of personnel 8. etc.).

# (b) The role of research: the share of investments devoted to it

In peak sectors, such as plastics, rubber and synthetic fibres. scientific research plays a very important part. The recent awarding of the Nobel Prize to Professors Natta and Ziegler for their work on polymerization catalysts helped emphasize this importance. The extremely extensive efforts which the leading chemical companies have made in developing new processes (3 to 5 per cent of their turnover in the United States) in connexion with the construction of large economic installations has led to the manufacturing of basic products such as ethylene, propylene and butadiene at very reasonable prices as well as to the development of several manufacturing processes for the same product (phenol, acetone, ethylene oxide, polyethylene, etc.).

#### (c) Competition

On top of this scientific effort is an extremely dynamic factor which is especially characteristic of the chemical and petroleum industries: competition.

Competition exists in various forms :

1. Manufacturers of petrochemical products are becoming more and more numerous (there are 3 to 4 times as many ammonia producers as in 1949).

2. Different intermediates can be used for the same manufacturing process: naphthalene and orthoxylene, and propylene with acetylene.

3. Different products have comparable uses. For example, cellophane, waxed paper, aluminium foil, polyethylene sheets and acetate film are all competing with each other.

This competition from all sides pushes prices down, which in turn opens up the way for new outlets and new applications.

#### (d) Prices and their development

Petrochemical product prices are above all characterized by their high level. Indeed, the price of finished products ranges from \$200 to \$500 per ton. Considerable efforts have been made to keep the prices of synthetic products within the range of those of natural products. Frequently, the only way to attain this goal has been by means of mass production.

Another characteristic of petrochemical prices is a relative stability, which does not exclude some fluctuations.

Some sectors (basic products, in particular) and some important intermediates undergo considerable fluctuations, generally downwards, but they never have the aleatory nature of those which affect natural products.

There are various reasons for this:

- In some fields the demand does not keep up with the supply, and the ensuing overproduction capacity results in temporary or prolonged dumping campaigns.
- Technical advances have enabled the prices of some products to be reduced either by improving conventional methods, or else by introducing new methods (acrylonitrile, phthalic anhydride).

#### Variations of market prices of the main petrochemical products

Listed hereunder are the current prices of petrochemical products, important intermediates and their derivatives.

The estimated price for each of these products is an average price which takes into account:

International prices published in various specialized magazines.

Transaction prices inside producing countries.

Prices quoted on the export market.

These different products generally have a more stable market price than that of finished products, except some of them which have registered notable drops during the last few years, such as, for example, benzene, naphtalene, phenol, acrylonitrile and methanol.

### ESTIMATED PRICES OF BASIC PETROCHEMICAL PRODUCTS, INTERMEDIATES AND THEIR DERIVATIVES

(US dollars per ton)

														1964	1960
Ethylene														100	
Ethyl alcohol .														200	
Acetaldehyde .														220	
Acetic acid														220	
Ethylene oxide .														340	
Glycol ethylene	۶.									÷			÷	300	
Amine ethanol	(m	iono		und	d	li)								460	
Acrylonitrile .														330	460
Styrene		• •			•		•							220	
Propylene	•	• •			•		•							54-60	
Isopropylic alcoh						•								150	
Acetone	•	• •	•	•	•	•			•					130	
Propylene oxide	•		•			•	•	•						340	
Cumene			•				•							220	
Phenol	•	•••	•	•	•	•	•	•	•	•	•			240	
Acetylene			•											240	
Vinyl chloride .	•													180	
Butadiene		•••	•	•	•	•	•							220-240	
Benzene														70	95
Dodecyibenzene														160	
Maleic anhydride														300	
Caprolactam											Ż			950	
0-xylene													•	126	
•					-	-	-		•	•	•	•	•		
Phthalic anhydrid									•				-	240	
P-xylene	• •	•	•	•	•	•	•	•	•	•	•	•	•	250	
Naphthalene	•		•		•	•	•	•	•					160	220
Methanol														60-70	90
Formaldehyde												•	·	180	~
	• •	•••	•	•	•	•	•	•	•	•	٠	•	•	100	

Figure 5 shows the price trends of the main products used as plastics during the last few years.

The same phenomenon occurred for acrylonitrile the price of which went from \$0.50 to \$0.33 per kg during the last ten years.

8



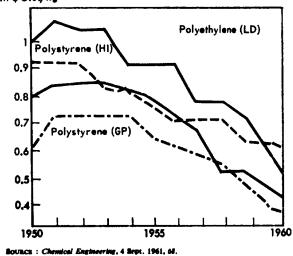


Figure 5. Price trends for the leading plastics from 1950 to 1960

Concerning the price of rubber, a decrease is going on in the price of SBR in Europe, and in France in particular where competition is very keen because of imports from the United States. The price in France is \$0.45 to \$0.46 per kg, whereas the U.S. domestic price is \$0.50 per kg.

The price of natural rubber has varied considerably during the last decade, and it is now stabilized at about \$0.52 to \$0.54 per kg.

Shell polyisoprene sells at the average price of natural rubber in the United States, i.e. \$0.55 per kg.

Polybutadiene, which is still a sought after product on the market, sells for 0.64 per kg. The starting up of several new units in the United States and in Europe brought on a price decrease of about 0.56 to 0.66 per kg.

It should also be pointed out that the price of rubber is international and that no tariff protection exists.

Concerning the price of ammonia, considerable changes can be expected starting now.

Ammonia having been exported in the form of nitrated fertilizer up to now, the price of ammonia delivered in small quantities has been \$90 to \$95 per ton. With the development of techniques of transportation and large capacity  $NH_s$  production unit construction, based on export market and erected in regions where the cost of natural gas and electricity is relatively low, it is now economically feasible to use ammonia as an intermediate which can be transported; and the availability of ammonia on the market in the near future means that a sharp price drop should take place, reaching an inclusive fob price of from about \$45 to \$50 per ton towards 1967-1968.

Table 4 shows the estimated prices for these different products in the next few years as well as the current prices.

TABLE 4 (\$ US/kg)

	1964	Forecasts (estimated)
Rubber		
Styrene-Butadiene	0.50-0.55	0.40
Ethylene-Propylene	0.66-0.57	0.50
Polybutadiene	0.66-0.60	0.55
Polyisoprene.	0.60	0. <b>50</b>
Plastics		
High pressure polyethylene.	0.38-0.44	0.37
Low pressure polyethylene.	0.55-0.58	
Polystyrene	0.40	0.33
Polyvinyl chloride	0.38-0.35	0.29

#### I.2.1.G. Problems linked to the production and transformation of finished products and 10 the sale of consumer goods

This category covers elaborated products such as the different polymers and the transformation products derived from polymers.

Manufacturing these products requires very large investments (cf. 1.2.1.A).

This sort of production can be helped along by the entrance into the market of a company which already produces these products and which can thus contribute its technical know-how and marketing experience.

Indeed, research on and application tests of these products require extensive personnel and equipment (cf. I.2.1.F.a), and furthermore, one must be willing to spend large sums of money to market the product.

Example: Typical pilot plant unit for manufacturing synthetic rubber

This pilot unit must be located near the synthetic rubber manufacturing plant; it should be able to process both emulsion polymerization and solution polymerization; it will represent an investment of between \$1 million and \$2 million.

It is operated by 12 engineers, 4 foremen, 15 shift operators and 4 standard maintenance workers.

Its operating expenses are about \$400,000 per year.

It consists of:

1. The catalysis unit designed for the manipulation, preparation, dilution and storage of the different catalysts.

2. The utilities generation needed for the proper operation of the units.

3. The Polymerization unit with several reactors and a control laboratory.

4. The finishing unit made up of the following sections:

Congulation and drying;

Compounding; Extrusion.

5. Stocks of products and of solvent.

#### I.2.1.H. Importance of market surveys

An important economic factor in the profitability of an installation is the rate at which it is made to operate once it has been built. Despite the apparently favourable aspects of a determined project, if the outlets have been badly calculated and the plant can operate at no more than 50 per cent of its capacity, it will obviously have difficulties competing with another plant which may be less advantageously conceived but which is able to operate at maximum or almost maximum nominal capacity.

The correct evaluation of the potential of a market and of its development is of capital importance in the success of a venture. This not only makes higher rates of production and lower unit costs possible, but it also makes possible a more efficaceous use of the investment capital which is extremely high in the petrochemical industry.

Another advantage which can be derived from a wellcarried-out market anal' is is is that of being in a position to opportunely foresee the regions or new products or new processes which mi ht prove profitable. The development of a market can, ir the long run, be just as important as its analysis, because it is by stimulating the interest of a consumer so that the makes wider use of products he already knows and so that he promptly adopts new articles that it is possible to supply the potential required for rapid growth.

#### I.2.2. RECENT DEVELOPMENTS

#### I.2.2.A. Processes

#### (a) Ammonia

Large-scale improvements in equipment, operating conditions, catalysts and unit control as well as in the fundamental knowledge of reactions have occurred in the production of ammonia during the last ten years (cf. chapter IV, Ammonia).

For example, the possibility of working under high pressure inside a steam reforming reactor has made possible, by reducing the size of synthesis gas compressors, a considerable decrease in investment costs. An identical, perhaps less noticeable, effect has been brought about by the utilization of new CO conversion catalysts.

Just recently, this important advance was extended to the manufacturing of synthesis gas from light and cheap petroleum cuts such as naphtha. The process developed by ICI can now process the naphtha in a reactor where pressure conditions are almost as great as for methane. Such a process is particularly advantageous for regions which have no natural gas but which do, on the other hand, have excess naphtha (this is the case, for example, in western Europe, Turkey and India), or which can procure uaphtha at a reasonable cost, due to :

Excesses which exist in some regions or which will exist in the near future;

Its low cost of transportation.

These advances have resulted in an extremely large drop in investment costs and operating expenses, and consequently they have considerably improved the cost price of this product. Use is no longer made of partial oxidation processes of the TEXACO type which had the advantage of being able to process extremely diverse feeds ranging from gas to very heavy liquid hydrocarbons such as fuel oil, but which required very costly air liquefaction units, thus considerably adding to the cost of the installations and the operating cost of the unit.

#### (b) The decline of acetylene

The competition between ethylene and acetylene, both of which have important common derivatives (PVC, acetaldehyde), is now turning in favour of ethylene. Indeed, in 1963 there were 13 ethylene units under construction or for which construction had been definitively decided upon, for a total output capacity of 1,130,000 T/year, and 8 acetylene projects totalling only 192,000 T/year.

This disfavour towards acetylene can be explained by the high price of this product as a direct result of the large amount of energy needed to manufacture it. Other factors in this trend are the recent advances which enable ethylene to be used more cheaply for manufacturing acetaldehyde (Wacker Process) and vinyl chloride (oxychlorination processes) and propylene for manufacturing acrylonitrile (Sohio and Ugine-Distillers Process).

# (c) Improving butane dehydrogenation processes

The old ethyl alcohol process has given way to the catalytic dehydrogenation of butane into butadiene (Houdry Process). Shell has announced an even more economical process of deriving butadiene from butane by the intermediary of iodinated derivatives.

#### (d) Revolutionary advances in rubber and fibres

High density polyethylenc, developed a few years ago, is enormously successful.

The appearance of stereospecific rubber is in the process of revolutionizing the synthetic rubber market. The competition between polybutadiene and polyisoprene has hardly begun but is already in danger of being upset by new products (ethylene-propylene rubber).

In the field of fibres, polyesters, acrylics and polyamides, considerable advances are being made.

#### I.2.2.B. Transportation

The implantation of certain industries near the cheapest energy sources has led to the establishment of large production units far away from consumer markets, and this has resulted in the expansion of maritime transport of basic products such as ammonia and butadiene.

This latter product in particular is shipped by sea. The plant of the Company: Les Elastomeres de Synthese in France receives its butadiene from the United States (Texas Butadiene) by ship (Iridina). Plans are being drawn up to build butadiene storage installations in Rotterdam.

Anhydrous ammonia produced in the plant built at Point-Lisas (Trinidad) by the Federation Chemical's Ltd., in which W. R. Grace & Co. is the leading shareholder, will mostly be shipped in the form of liquefied gas to various countries by means of tankers built specially for this purpose.

The plant will be able to produce 235,000 tons of anhydrous ammonia per year. It is located and conceived to enable large tonnages of liquefied ammonia to be shipped for the first time by boat to various countries where it can be used directly as fertilizer or as the main component of nitrogen solutions and solid composites such as urea and ammonium nitrate. Up to now, ammonia has been transformed into solid fertilizers (sulfate and ammonium nitrate or urea) before being shipped. This new technique of distributing ammonia constitutes an extremely important advance in the potential supply of raw materials at low prices in countries where it has not heretofore been possible to manufacture ammonia because of the lack of raw materials or where it has been prohibitive because of the limited nature of the market.

The output of the plant will be shipped in two tankers built specially to transport either a load of anhydrous ammonia at - 32° C or a load of refrigerated propane at - 42° C. The ships will transport their load of ammonia or liquefied gas in four individually insulated holds. An inert gas will circulate between the holds containing the load and the secondary reservoir. This gas, nitrogen, will purge and clean the reservoirs so as to enable other types of loads, such as propane, to be carried on the return trip or else to enable the ship to be sub-chartered. The propane transport capacity is 80,000 barrels. The four holds of each ship have a total capacity of 9,000 tons of anhydrous ammonia with a density of 0.68 at - 33° C. Each ship can transport nearly 300 tons of dry cargo in its holds, such as solid nitrogenous fertilizers in the form of urea or ammonium sulfate.

The island of Trinidad was chosen as the location for the plant because it is one of the rare parts of the world where inexpensive natural gas is found in immediate proximity to the high seas. Similar conditions can also be found in certain Middle Eastern countries. However, it should be noted that installation investments of this sort would be higher in the latter region because of the fact that it is far away from sources of equipment.

#### 1.2.2.C. Unit size

Units are constantly increasing their output capacities in an effort to lower the cost price. This is true of ammonia where the capacity of a unit (i.e., the reactor) is currently 600 T/day, while 1,000 T/day units are being studied. The same is true of ethylene units which now have a capacity of 200,000 T/year or more.

The result, for basic products at least, is that a theory of minimum economic capacity has been established which obliges larger and larger units to be built in order for them to be competitive.

It is worth mentioning, however, that this phenomenon is less noticeable for the transformation of basic products into finished products. The nature of the equipment and the parcelling out of manufacturing activities do not lend themselves so well to giganticism.

## Part II. General economic conditions and basic principles : the bases for establishing a petrochemical industry

## **II.1. ECONOMIC FACTORS**

Elements of operating cost of installations and manufacturing cost of products.

These elements contribute in determining the operating cost of units and in calculating the manufacturing cost of products. They depend upon specific conditions prevailing in different industrialized or developing countries. Their analysis is of prime importance for it constitutes the basis of different studies to be undertaken when establishing new industrial projects.

They include: cost of raw materials; cost of utilities (steam, electricity, fuel, etc.); cost of labour and supervision; cost of construction; and taxes.

In this chapter each of these elements will be analysed and discussed thoroughly. Emphasis will be put on the differences existing between different countries.

In the second part of this report, while studying various petrochemical productions, all the above economic factors related to specific projects in different specific areas will be taken into consideration when determining their economic importance.

#### II.1.1. COST OF RAW MATERIALS

#### (a) Natural gas

The price of natural gas is usually known at the well head. Its price when delivered as a raw material to a petrochemical plant depends on several factors such as:

Location of consuming centres (which enables the distance from the well to the plant to be evaluated);

Amounts consumed (which enables the diameter of the pipe line to be determined);

thus making it possible to calculate the cost of transporting natural gas from the fields to consuming centres.

This cost is quite low in the case of large quantities transported over rather small distances. It gets higher, when the rate of flow is low or when the distances are very long and it becomes very high if special liquefaction facilities and liquid methane transportation in special refrigerated tankers like "Methane Princess" and "Jules Verne" are considered. If adequate port facilities do not exist, their cost should be taken into account when calculating the transportation cost of natural gas.

Prices of natural gas in different countries, are given hereunder at field, sea coast and consumption contres.

## GAS PROM LACQ (FRANCE)

															*****
At	Pardius (5	km	fr	0fi	t	he	1	e k	I)						1.36
At	Toulous			•		•	•	•							1.70
At	Lyon		•	•	•										2.56

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#### GAS FROM HASSI-ER-R'MEL

	Domestic market \$/m <sup>9</sup>	Exportation ¢/m²
At the field	0.36	0.54
	0.67	0.85
At Algiers or Oran <sup>b</sup>	0.77	
At Toulouse *		1.70
In United Kingdom 4 (liquefied)		2.50

				¢/m*
• Cost of transportation	by	pipeline.	Hassi-Er-R'Mel-	<b>\$(m</b> )
Arzew				0.31
Cost of transportation Algiers or Oran	by	pipeline,	Hassi-Er-R'Mel-	0.41
· Costs of transportation				
Toulouse				1.16
<sup>4</sup> Cost of liquefaction at Arzew-United Kingdom, appr	Arae oxim	w + cost ately	of transportation	1.60

ITALY \*

	As fuel \$/m²	As c <b>hemiosi</b> foodstock \$/m <sup>2</sup>
Northern Italy	1.70	1.00
Southern Italy		0.80

Paper delivered at Institut Economique et Juridique de l'Energie;
 Seminaire 63. University of Grenobla, 26 April 1963.

	100	
L	181	

Gulf Coast (chemical	feedstock)	 	. 0.70
East Coast (chemical			

The attractive low price of Algerian gas is due to its exportation as liquid methane in very huge quantities which enable production and transportation costs to be cut.

The very low price of natural gas in the United States (Gulf Coast) is due to the proximity of fields and to the high level of demand; however, this price tends to increase and it is estimated that it may reach  $1 \notin m^a$  by 1970. The price on the East Coast is much higher because of transportation costs.

In Italy, raw materials for petrochemical industries are offered at low prices, particularly in the south, so as to encourage industrial development and to attract investors in order to raise the standards of living of this less favoured region of the country.

In the West Indies, particularly on Trinidad, natural gas is available for industrial uses at about 0.200 m<sup>6</sup> at the field.

This low price, to which must be added:

The possibility of nearby port facilities existing.

The proximity of very large ammonia consumption centres has been sufficiently attractive to investors in petrochemicals to warrant construction of a 235,000 T/year ammonia unit.

Such low prices may be encountered in other areas, particularly in the Middle East and Libya, and may be the starting point for the development of petrochemical industries there.

#### (b) Liquefied gas

Current prices are as follows:

	U	SA	
	Gulf coast	East coast	Europe
	(\$/ton)	(\$/ton)	(\$/10n)
C	17-22	44	. 37
C	18-24	37-46 j	
C4	22-26	31-40	37 (household uses) 28-30 (petrochemical uses)

Prices of liquefied gas used as raw materials for petrochemicals depend mainly on the quantities consumed, that is on possible markets for petrochemical products based on L.P.G. In developing countries when L.P.G. may be available in large quantities, possibilities of exporting propane and butane may help to lower costs of recuperation and of transportation from fields to the coast. This may be quite important because the petrochemical industry consumes rather small amounts of such feedstocks: a butadiene unit of maximum size (70,000 T/year) with a single stream of reactors would consume 135,000 T/year of butane; an ethylene unit of 150,000 T/year of ethane.

#### (c) Liquid hydrocarbons: naphtha and condensate

Naphtha is available in Europe and in many other countries such as India whose consumption is largely based on middle distillates such as kerosene and gas oil.

Condensate is produced in association with natural gas. At Hassi-Er-R'Mel (Algeria) for example, 400,000 T/year will be available when gas production reaches 2 billion m<sup>2</sup>/ year (end of 1964).

The price of naphtha in Europe may be estimated at about \$16 to \$20/ton. These attractive conditions (availability of large quantities, low prices) have been behind the recent growth of the petrochemical industry : ICI in Great Britian and SNPA (in association with Solvay and Rhône-Alpes) in France, are considering the construction of very large steam cracking units (1 million tons/year) of naphtha at Feyzin, France, based on such raw materials.

#### II.1.2. COST OF UTILITIES

The petrochemical industry is a rather large consumer of electricity. The power consumed is about 15,000-20,000 kW for an ammonia or a butadiene unit of medium size.

In industrialized countries, power is often produced in very large thermal or hydro-electric power stations, and it can be purchased at different rates from one country to another depending on the power consumed and length of utilization. In France, the average price would be about 1\$ kWh; whereas in the United States, power (hydroelectricity) may be purchased at about 0.3-0.6\$ kWh.

If power is not available, it must be produced within the petrochemical plant itself. Its cost would then depend,

as for manufactu ing units, on the cost of construction, price of fuel (natural gas, fuel gas, fuel oil), cost of labour, etc., and would change from one country to another.

The costs of power produced by steam expansion in back pressure turbines in different countries are given hereunder:

United States Gulf	Coast	 	 	0.71 - 0.91 ¢/kWh
United States East	Coast	 	 	0.81 - 1.0 ¢/kWh
Common Market .		 	 	1.0 ¢/k₩h
Japan	• • •	 •	 • • •	1.0 ¢/kWh

The same is valid for the cost of steam and cooling water which are usually produced in the plant itself.

#### II.1.3. COST OF LABOUR

The cost of construction labour in developing countries is usually higher than in industrialized countries, although wages are lower. This is due to several factors such as: lower productivity, and lack of qualified technicians and skilled workmen (such specialists would have to be imported from abroad at very high cost).

It is difficult to specify the real maintenance and operational labour costs for the manufacturing units of a specific plant without going into details. Nevertheless, taking into account the following factors — training of local operators, foremen and engineers, and import of foreign technicians — one may reasonably consider that there will be an increase of about 30-50 per cent compared with industrialized countries, at least during the first years of operations.

The comparative costs of labour in different countries are given hereunder (I.E.C., vol. 54, no. 3, March 1962):

United	Stat	86										,		1.00
United	Kie	<b>ek</b>		•	•									0.69
Itely .	• •										•			1.35
Mexico														1.54
Brezil	• •													1.23
Australi														
Canada														1.08
Prance														0.81
<b>Pedera</b> l	Re	pub	lic	0	r (	Ge	Les.	Ŋ						1.68
Jepen														

This comparison takes into account the standardization of equipment, work schedule, productivity, degree of mechanization and duration of work.

#### **II.1.4. CONSTRUCTION COSTS AND FINANCING**

The cost of construction in different countries may vary considerably depending on different factors such as: Cost and availability of equipment,

Equipment specifications and construction standards, Cost of transporting equipment when it is not available at the site.

Cost and availability of labour,

Cost of foreign labour when required,

Productivity and duration of construction.

When comparing construction costs in industrialized and developing countries, it can readily be seen that several factors intervene to make it higher in the latter countries.

#### 11.1.4.A. Factors influencing construction costs

#### These are:

Long-distance sea transportation of all or part of principal equipment (which constitutes in value about 80 per cent of total cost of equipment) if it cannot be manufactured locally,

Insurance cost during transportation,

- Overland transportation cost if the plant is not located on the coast,
- Import duties levied on imported equipment,
- Construction and engineering costs are higher (because of imported foreign labour),
- The cost of construction done by local companies is higher.
- Local conditions: duration of construction is usually 1.5 or 2 times higher in developing countries than in industrialized ones.

Table 5 hereunder lists the different items in the cost of a plant and gives, as an illustration, an estimate of the probable lost of a plant built in North Africa or in India compared with the cost of an identical plant erected in France.

TABLE 5. ESTIMATE OF COMPARATIVE INVESTMENT CORPS

				 Prance (m % of solal)	North Africa 1 as % of cost in	
Equipment .				62	63	66
Erection				18	23.5	25
Civil works.				5	5.5	6
Engineering.				13	14	15
				100	111	121

In developing countries it is often necessary to provide supplementary investments in order to secure normal operation of the plant and which are not usually considered by local organizations. These cover:

Housing of personnel and their families,

Installation of utilities: power, steam, water, etc.,

Transportation facilities,

Port installations.

Estimate of comparative construction costs in different countries is as follows:

France																				200
United	Stat	<b>66</b> .																		100
United	Kin	gé.		•	•	•	•	•	•											95
haly .	· ·		•	:		•	·	•	•	•	•	٠	•	•	•			•	•	
	Rep		<b>B</b> 4			. A.		17												100
Delgium	• • •	• •	• •	•	·		•	•	٠	•				•	•	•	•	•		- 100

Algeria									111
Turkey (at coust)									115
Iran (at coast)									116
India (at coast) (inland)								1	121
iniand)								i	125

It should be emphasized, moreover, that the above figures are only intended as general estimates, and they may not be valid in some particular cases. Still, they can be considered as representative in most cases.

#### 11.1.4.D. Factors influencing ways of paying for the installations

Financing the construction of a plant in a developing country would result, if compared with the construction of the same plant in Europe or the United States, in some additional expenses and supplementary risks. Most of these risks are usually covered by insurance, the cost of which is added to the price charged to the buyer. The risks which may not be covered by insurance are evaluated by the seller and also included in the price of the plant. The same is done with other expenses such as prefinancing, reimbursement of loans and all other bank operations if payment is not in cash and if financing is asked for by the companies in charge of construction

## (a) Cost of prefinancing

In the following standard cases :

- Profinancing covoring 3 years between signing the contract and starting up the plant;
- During this period payments to construction companies would be spread out as follows: 10 per cent down; 30 per cent during construction; and 10 per cent on definitive approval.

Six per cent interest rate.

Cost of prefnancing would be 4 per cent of the total investment.

In cases where a plant is paid for in cash, this supplementary sum is paid directly by the owner. In cases where the construction of a plant is financed, the controlling enterprise adds this sum to the initial investment planned on.

#### (b) Cost of financing

The following conditions are usually accepted by general contractors and may be considered as possible: No payment on signature of the contract;

No payment at start-up (3 years later);

Payment starting 6 months after start-up;

Reimbursement over 10 years by payments every 6 months.

The additional costs resulting from such conditions are usually included by the contractor in the total cost of the plant:

These additional costs 1 are due to:

Costs of insurance covering risks of loans to foreign countries;

Guarantee against inflation;

#### Bank expenses;

Risks attached to the part of the loan not covered by guarantee;

No shopping around.

The above factors also affect the cost of imported equipment as well as engineering and construction. Table 6 hereunder shows the influence of prefinancing and financing on the cost of various investment components.

TABLE	6.	INFLUENCE	OF	PRI	PIN/	ANCING	AND	FINANCING	
		ON	CO	ST	07	UNDS			

	Personiago of Imported oquipment of	Parcensage of ongineesing and construction	Percentage of local expeñses
Professions			4
	•	•	•
Planning			
Incurance	4	4	
Risk of inflation	2	2	
Bank expenses	0.5	0.5	
Risk of non-guaranteed			
loans	4	4	
No shopping around	4		
	15.5	•• 5	4

In order to calculate the total cost of a financed plant, the above supplementary charges should be added to those resulting from the fact that construction is done in a developing country (cf. II.1.4.A.).

"No shopping around" has not been taken into consideration for engineering and construction where it is assumed that open competitios could have an effect.

Table 7 gives the probable cost of a financed plant in North Africa (Algoria, Tunicia, Morocco) and in other countries on the Indian Ocean (India, Pakistan, Ceylon) compared to the cost of the same plant in Europe or in the United States.

#### II.2. CALCULATING THE PRODUCTION COST OF PETROCHEMICAL PRODUCTS

In order to compare different projects and production costs of petrochemicals, a standard method of calculation should be adopted, taking into account the specific characteristics of each unit and specific consomic factor for each country (af. II.2 and figure 6).

This type of calculating many be done in two stops:

<sup>&</sup>lt;sup>3</sup> Internet on Jonne is not included in total investments. The contraponding expansion are included in the practy expanses of the plant and make up part of the production cast of graduate (cf. (J.)).

	Coor of a plane built in Burape as due	Cost of a j in North Afric		Cost of a plant built in a country on the Indian Ocean (In a port)					
	United States (cash payment)	Exchange currency (with Anancing)	Local currency (cash payment)	Exchange currency (with Anancing)	Local armine				
Equipment.	62	55		55	11				
Construction	18	12.5	11	13.5	11.5				
Civil engineering	5		5.5	- 480.0	6				
Transportation.	2	5		9	_				
Engineering	13	14		15	-				
Sub-total	100 %	86.5	24.5	92.5	28.5				
		111	%	121	%				
Profinancing * Financing * of import-		3.5	and a second sec	3.7					
ed equipment cif Financing * of com- struction and engi-		10.8	_	11.4	_				
neering fees (includ- ing civil engineering)		3.5		3.7					
		104.3	24.5	111.3	28.5				
TOTAL	100 %	128.8 or	129 %	139.8 or	140 %				

#### TABLE 7. ESTIMATE OF THE PROBABLE COST OF A PLANT BUILT IN ALGURIA OR INDIA, TAKING PENANCING INTO ACCOUNT

\* Estimated at 4 % of the investment (of. I.1.4.B.a).

\* The multiplication factor is 100/100 — 15.5 = 1.18 for the imported equipment of (of, table No. 6).

\* The multiplication factor is 100/100 -- 11.5 = 1.13 (cf. table No. 6).

#### 1. BANC DATA

(a) Determinating technical data of processes involved: Yis.da, material balance, consumption of raw materials and production of by-products:

Concumption of utilities: electricity, steam, fuel, cooling water and process water;

Consumption of chemicals and catalysts:

Labour and supervision.

(b) Determinating economic data of processes involved:

Cost of investment, including:

Manufacturing units;

Off-sites such as storage and utilities generation;

Royalties;

Initial charge of estalysts and chemicals;

Start-up expenses;

Working aspital severing expanses for row materials, utilities, cetalyste, eleminate and labour over some parted during which the value of the products sold is not coulded to the plant (stored products or time poyments, for example).

The following items may also be included in the investment figures for petrochamical plants: Purchase of land;

Spare parts;

Initial expenses;

Participation in the expenses of housing and training personnel;

Interests during construction.

### 2. CALCULATING OPERATING COSTS

The operating cost of petrochemical production may be divided into two parts: variable charges and fixed charges. Variable charges are proportional to the rate of production of the unit (per cost of nominal especity). Fined charges, on the contrary, depend directly on nominal capacity and the total investment.

#### (a) Variable charges

They include:

Exponess for row materials;

Expenses for utilities concemption : electricity, steam, fuel, cooling water, process water ;

Expenses for catalysts and chemicals;

Expenses for labour;\*

<sup>&</sup>lt;sup>2</sup> Although they do not actually increase proportionally to the expanity but racher like the fixed changes, they can, severtheless, to included in the variable changes.

Royalties (which may be included in the investment figure or paid as running fees over 8 to 10 years).

## (b) Fixed charges

They include :

Amortization of the plant and financial charges:

Amortization expenses vary from one country to another; some average rates usually accepted during the first five years of running a plant are given below for different countries:

										of Investment
France										15.3
United	States						•			12
United	Kingk	ЯŇ								18
Italy .										18
Pederal	Roput	Hic	of	G	ner	Ŋ				13

Financial charges include interests on short or long term loans and dividends from shares which constitute the actual capital of the company : Maintenance expenses which usually amount to 4 per cent of the production units and general installations,

Plant overhead expenses, general overheads and sales expenses,

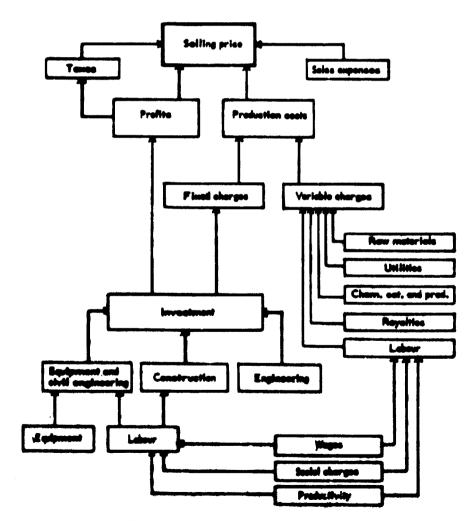
Interest on working capital which is usually 5 per cent.

Note: Calculations of production costs of different petrochemicals (cf. II.2) will be based upon nominal unit capacity. It can be seen that if the fixed charges remain unchanged, production cost will increase proportionally to the decrease in the rate of operation of the units.

#### II.3. BASIC PRINCIPLES: THE BASIS OF CARRYING OUT PETROCHEMICAL PROJECTS

Although it is often possible, from a technical point of view, to produce most petrochemicals starting from available raw materials and to envisage setting up s petrochemical industry based on market demands, it is

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Pane 6. Resoluting the selling price of produce

nonetheless of prime importance that such projects should meet the following economic criteria:

I. Such plants should correspond to the real needs of the country and produce consumer goods at reasonable prices so that they are accessible to as wide a market as possible,

2. The plant must be built under conditions such that it contains within itself the conditions necessary for its subsequent expansion.

To meet the above criteria, the following conditions should be fulfilled:

1. Setting up a price ceiling not to be exceeded by local productions. This limit may be based on market prices in industrialized countries (cf. 1.2.1.F.d.), multiplied by a moderate tolerable coefficient.<sup>4</sup> This coefficient changes from country to country, but prices of local production should always be lower than or equal to prices of imported products.

2. Net profits should be high enough to provide for:

Reimbursement of invested capital within a reasonable period, taking into account the rapid evolution of technology;

Maintenance of units, development of production and expansion of the plant.

# II.4. ESTABLISHING THE SELLING PRICE OF PRODUCTS

Figure 6 shows the influence of different parameters affecting production costs and points out the different economic factors which, when added to the production cost, enable the selling price to be determined.

These factors are:

Profits;

Taxes;

Sales and distribution expenses.

Profits are fixed by the annual rate of return on the total investment (U per cent), which equals 1/T, T being the pay-out time, i.e. the period during which total investment (A) is recovered.

The net cash flow (V) will then equal A.U./100. The net income after taxes or annual act profit (W) is obtained by deducting the amortzation (M) from the net cash flow (V), since it is already included in the production cost (W = V - M).

Since the tax rate on profits is  $(\theta)$ , the net income before taxes or gross annual profit (X) would be:

$$\mathbf{X} = \frac{100 \text{ W}}{100 - 6}$$

The selling price (Y) is obtained by adding production cost (S) to gross annual profit (X)

# Pay-out time and profits

# Because of:

- The constant increase in the cost machinery and equipment,
- The very rapid evolution of technology which greatly increases risks of premature obsolence of processes or products, a pay-out is generally admitted which enables a corresponding profit to be realized at an annual rate or return on investment of 20 per cent (instead of 15 per cent for legal amortization in France). This profit corresponding to a pay-out time of 5 years would enable the loan for financed plant to be reimbursed, and it can be employed to finance new projects.

#### Taxes on profits

These vary from one country to another. The average tax rates for various countries are given below:

																	Personage of profile
United	Su	lte	8														52
France																	50
United	Ki	ng	da	m	•												53.75
Federal	Re	ep/	ub	lic	0	f	Ge	T	na	ny							51
Italy .	·	·	•	·	•	•	•	•	•	•				•			35
Japan .	•	٠	٠	•	•	٠	٠	•	•			•					50
Canada	•	·	·	•	·	•	·	·	•	·	•	•	•	•	·	•	41

Table 8 gives an example of how the selling price of a product is calculated in industrialized countries on the basis of the following generally accepted conditions :

Pay-out time .			•							5 years
<b>Lates on profits</b>										50 %
Amortization .	•	•	·	•	•		•	•		12.5 % of investment

#### TABLE 8

Investment (A)	\$ 2,000,000
Amortization (M)	= \$ 250,000
Production cost (S)	• 200,000
(T) Pay-out time	5 years
(U) Rate of return on investment	20 %
(V) Net cash flow $\frac{(A)(U)}{100} = \frac{A}{5}$	- \$ 400,000
(W) Net profits after taxes (V) - (M)	- \$ 150,000
(X) Net profits before taxes $\frac{100 \text{ (W)}}{100 - 50}$	\$ 300,000
(Y) Selling price $(X) + (S)$	= \$ 300,000 + (\$)

## Part III. Factors conditioning the creation of a petrochemic... industry -- ensuing limitations and means of remodying them

The promoter of a petrochemical investment can be animated by several types of considerations such as:

1. The market, if the individual involved is a chemist who sees a rival product developing and who wants to preserve his outlets.

<sup>&</sup>lt;sup>9</sup> This coefficient may be estimated at about 1.15 to 1.30 (United Nations BCAPE Conference, Toheran 1 to 15 Sept. 1962, Installation of a petrochemical industry in a developing country. Presented by the Institut Prançais du Pétrolo).

2. The availability of raw materials, if the individual is a refiner (crude hydrocarbons or by-products from their being processed).

3. The possibility of valorizing by-products of the planned manufacturing so as to reduce production costs.

All or several of these factors usually come into play simultaneously when making decisions, and this is why, as we say in Chapter I, petrochemical manufacturing units come into being within the framework of complexes where the different production activities support one another within the interior of integrated structures, or, at any rate, supplementary associations.

However, it was noted concerning progress made in the field of transportation, that there was a certain tendency towards setting up an international market for certain major products such as ammonia or butadiene. It should also be pointed out that there are usually large excess production capacities for these major intermediates (the units now operating are working below capacity and, consequently, it would be possible to increase production in all fields without having recourse to additional investments). Therefore, it is eminently desirable that a petrochemical products manufacturer be certain of:

1. A minimum consolidated outlet, enabling him at least to amortize his installations, and

2. A reliable source of supply.

The problem for developing countries is to determine, in the midst of current tendencies, what the motives may be for establishing such an industry on their land.

# III.1. FACTORS CONDITIONING THE CREATION OF A PETROCHEMICAL INDUSTRY

# III.1.1. SIZE OF OUTLET MARKETS

Consumption increases are relatively easy to foresee on the basis of tendencies noted during past years and from the development of consumption in other countries where the standard of living is the same or slightly higher. Predicting the development of the production capacities of other countries is somewhat more aleatory. Indeed, plans are often drawn up in great secret. Furthermore, it is relatively difficult to evaluate the degree of certainty in the completion of a given project announced by its promoters. The creation of a petrochemical industry in developing countries is conditioned by a very careful preliminary evaluation of its current and future market and of its potential export outlets. These market surveys are of major importance, and it is essential that they be done before planning any industrial project.

# III.1.2. LOCATION OF MARKETS --- TRANSPORTATION PROBLEMS

The geographical location of potential markets for: 1. Raw materials (naphtha, natural gas, liquefied gas),

2. Intermediates (ethylene, ammonia, butadiene, etc.) and finished products,

which might subsequently be manufactured in the developing country, generally have to allow for an itinerary over which these products must be transported (by land or sea). The influence of transportation costs on the C.I.F. price of products is thus important.

# Transportation of raw materials and petrochemical products

Transportation costs are very different for gaseous and liquid hydrocarbons. Whereas they are fairly low concerning naphtha, condensate or other heavier products, they are higher concerning  $C_1$  and  $C_9$  gaseous hydrocarbons which are transported in high pressure cylinders, or concerning liquefied hydrocarbons which are transported in special ships (methane tankers, for example), or concerning  $C_9$  and  $C_4$  liquefied gas, as well as concerning certain petrochemical products such as butadiene and ammonia which are transported liquefied in refrigerated ships under atmospheric pressure.

Liquefaction and storage units corresponding to the capacity of the ships used for transportation must also be planned at both the points of arrival and departure of the products.

In order to specify the differences which exist between the cost of transporting different products, some of the elements of the cost of transporting hydrocarbons and chemical products are given below:

# Condensate and naphtha •

Const of	Algeria	Marseille,	France						\$1/100
Const of	Alexanda	T				•	•	•	41/1011
Coast of		London,	United	King	dom				\$2/ton

which is, respectively, 5 % and 10 % of the cost of the naphtha.

## Natural gas

Coast of Algeria -- London, United Kingdom, transport of iiquid methane by methane tanker \$1.60/m<sup>3</sup>

which results in the tripling of the FOB methane price.

## Liquefied gas

The utilization of refrigerated ships for transporting liquefied gas leads to considerable savings compared with the utilization of high pressure ships which is the method most widely used up until quite recently.

· Intascale -- including 20 % discount.

Figure 7 (below) shows the influence of the size of refrigerated ships on the transportation cost of liquefied gas in (SU.S. per ton) from Freeport, Texas, to Antwerp, Belgium. Storage on departure and on arrival is not included in this cost:

Chemical products: ammonia and butadiene

- The cost of transporting these products is about the same as for liquefied gas given tankers of the same capacity and the same distances to be covered.
- The cost of transporting butadiene from Texas to the Etang de Berre in France by 6,000 to 8,000 ton ship is \$9.20/ton (not including storage on arrival and departure).

- Two refrigerated ships capable of carrying approximately 9,000 T/year of ammonia are now being built for W. R. Grace & Co. by the Marine Transports Line Inc. in New York. It is estimated that the cost of transporting ammonia across the Atlantic in boats of this capacity will be about \$6 to \$8 per ton.
- The cost of transporting ammonia varies with the capacity of the refrigerated ships.

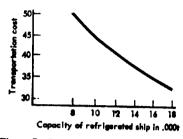


Figure 7. Cost of transporting liquefied gas (assuming 100 % utilization of the ship)

For ships with respective capacities of 1,700, 2,000, 2,200 and 2,500 tons and making a run of 1,200 kilometers, the estimated transportation cost is, respectively, \$7.60, \$7.40, \$7.20 and \$7.00 per ton of ammonia (compared with the above mentioned cost for 9,000 ton ships crossing the Atlantic).

It also varies with the distance covered.

For example, for 1,700 ton ships covering, respectively, 1.200, 2,400 and 3,000 kilometers, the estimated transportation cost is, respectively, \$7.60, \$12.60 and \$14.40 per ton.

NB. The cost of transporting ammonia has a big effect on the price of this product.

Ammonia FOB Trinidad Transportation Trinidad Europe (by 9,000 ton ship) Cost CIF Europe										
which is an increase of 19%	50									
Ammonia EOB This is a	\$/ton									
Ammonia FOB Trinidad	42									
(A) 1,200 km	7.60									
(B) 2,400 Km	12.60									
(C) 3,000 km	14.40									
Ammonia CIF	·									
For (A)	\$/ <i>le</i> m									
For (A)	49.60									
For (B)	54.60									
Fur (C)	56.40									
which is an increase of 18 % for (A)										
which is an increase of 30 % for (B)										
which is an increase of 35 % for (C)										

Concerning butadiene, which is already a very elaborate product, the CIF selling price in Europe is not very different from the FOB price on the Gulf Coast, even despite the high cost of transportation across the Atlantic.

ROB																\$/ <i>1em</i>
FOB price	٠	•	•	•	•	•	•	•	•		•	•	•			220
T LINE DOLUTION	•	•														A 10
Core, hanne	٠	•	٠	•	٠	٠	•	•	•	•		•				229.20
which is an is	ACI	101		0	(4	19	4.									

111.1.3. INFLUENCE OF AVAILABLE RAW MATERIALS ON THE KIND OF PETROCHEMICAL INSTALLATIONS OR COMPLEX TO BE ESTAPLISHED

Large quantities of natural gas and gas associated with crude oil are produced in the United States, the Soviet Union, the Middle East, North Africa, Pakistan, Central America and Europe. They are the basis for the development of the petrochemical industry in the United States which utilizes methane and liquefied gas such as ethane, propane and butane as raw materials. Because of the extensive refining capacities and the extremely high gasoline market (45 per cent of the crude oil processed) the United States also produces a large amount of refinery gas which is one of the raw materials for the petrochemical industry.

In Europe where the gasoline market is comparatively smaller (25 per cent of the crude oil processed), refinery gas is not produced in sufficient quantities to enable the petrochemical industry to develop, and the excess byproduct gas from refining operations is the most plentiful source of raw materials. Refinery gas is, however, utilized, as is natural gas (Ravenna in Italy, and Lacq in France). New discoveries of natural gas in the Netherlands and in North Africa and the transportation of liquefied gas which would enable large quantities to be imported from the Middle East, Libya and Algeria would enable much wider utilization of L.P.G. in replacement of naphtha.

Natural gas and gas associated with crude oil can, for developing countries which have them, constitute an important factor in the establishment of a petrochemical industry.

For countries where such raw materials are not available, sources of supply could be found in:

#### Refinery gas;

Excess naphtha (India, Turkey etc.).

Indeed, the market for middle distillates is extremely large in these countries (exactly the same problem on the European market), and the small market for gasoline leaves quantities of naphtha available on the market at an advantageous price for the petrochemical industry. When the refining capacity does not make it feasible to plan the establishment of a petrochemical industry based on refinery gas or naphtha of which there are insufficient quantities, steps will have to be taken to import naphtha, for which transportation costs are low, in order to produce basic petrochemical products, or else provisions will have to be made to import basic products such as ammonia, butadiene, etc., which are at the start of finished products industry.

In the light of the elements described above (cf. III.1.2), petrochemical manufacturing can be envisaged starting from the different kinds of raw materials available.

(a) The cost of transporting naphtha and condensate is relatively low, thus making it more advantageous to plan on implanting a petrochemical unit which uses this as raw material near the point of consumption rather than at the point of production. Indeed, the additional expense entailed in transporting raw material is not large enough to compensate for the ensuing advantages of the proximity of the market, of the greater case there would be in raising capital and financing, and the possibility of selling or utilizing all of the by-products.

(b) The cost of transporting gas such as methane, ethane and propane is higher, meaning that exporting them to other countries for use as possible feeds for the petrochemistry industry can only be envisaged as a supplement to already existing raw materials or to liquid hydrocarbons.

- Methane transported in this way cannot compete with naphtha as a raw material for manufacturing synthesis gas and producing ammonia or methanol.
- Ethane and propane cannot compete with naphtha as a feedstock for producing olefins.

On the contrary, however, these products can be utilized as a raw material for petrochemistry or other industries at the spot where they are available for the following reasons:

- The reserves are usually abundant and provide long range supplies of raw materials.
- Despite the cost of their recuperation and fractionation, lt is hoped that they will constitute an inexpensive raw material.
- Petrochemical products, which can be produced from these gases, offer technical and economic advantages compared with identical productions produced from naphtha.
- Methane is the best feed for producing ammonia. Steam reforming of methane is a less costly process than that of naphtha, both from the point of view of the amount of Investments needed and the operating cost.
- The same is true for ethane and, to a slightly lesser degree, for propane with regard to the production of ethylene and propylene.
- Ethane and propane cracking is more selective than naphtha cracking.

					,	-	•					Perce weight of	niage leinney for
												Interiore	Propolone
Ethene .	•	•	•	•								82	
Proyane Naphtha	•			•								42	23 16-18

There are no by-products such as the  $C_4$  hydrocarbons and gasoline which intervene and decrease the efficiency of the operation if they are not valorized.

However, the following points should be borne in mind. Whereas ammonia is an intermediate which is advantageously transported for the reasons given above (cf. II.2 and the figures given below), the problem of transporting  $C_a$  oldins by refrigerated ship has not yet been solved in a satisfactory and economic manner.

The ratio of transportation cost (including handling) of ammonia to that of nitrogenous fertilizer (per ton of nitrogen) is shown below:

Ammonia (82 % N) .																	1.0
	- 76-																
Usea (46 % N)	•	•••	•	•	•	٠	•	•	•	•	•	•	•	•	•	•	2.5

As a result, the production of olefins should be followed up by installations which would make allowances for more elaborate and more easily transportable products such as: monomer and polymer vinyl chloride, polyethylene and acrylonitrile.

The problems then posed by the manufacturing of these products (polyethylene in particular) and concerning: the size of investments, the production efficiency, and the search for a market, are of prime importance, and associating with a private company already installed on the market would help in solving them.

(c) The cost of transporting butane (as potential butadiene) should be about the same as for butadiene. Therefore, it is difficult to plan a future implantation without making a detailed study of an individual case. It can be assumed, however, that the proximity of a source of inexpensive natural gas for a unit for the dehydrogenation of n-butane into butadiene (a unit which consumes a lot of energy) is a favourable element in implanting such an industry in a country having large reserves of liquefied gas.

# III. I.4. INFLUENCE OF COST OF ENERGY AND RAW MATERIALS

In Part II it was seen that the cost of natural gas can be very low in some developing countries and that this advantage can also favour the establishment of a petrochemical industry. This attraction varies, however, with manufacturing processes, depending on whether they are more or less large consumers of energy. Manufacturing major intermediates requires a lot of energy.

	Ammonia ex-methane	Dutadiene 13-butane	Eskylene ez-othane	Acetylene ex-methane
Cost	540 to \$50/T	\$200/T	\$80/T	\$220/T
Natural gas and raw material consump- tion	8	6.2	32	48
Share of energy and raw material in the				w
cost	16 to 20 %	25 %	40 %	2%

On the other hand, the production of derivatives of these basic products requires relatively little energy, in that the cost of manufacturing them mainly consists of personnel and amortization expenses. The advantage of manufacturing them in developing countries is obviously appreciable and useful for the development of the country, but the decision to implant them comes up against obstacles which should not be underestimated in the beginning.

These products are more and more elaborate and diversified, and the difficulties involved in manufacturing them (high degree of technicity of the installations and of the personnel), the diversity of buyers (delicate and finetuating market) and even the investment rate per ten produced, all point towards the implantation of such an industry within the framework of an industrial complex which is already diversified and which is located in a highly developed consumer region (cf. I.2.1.D). Whereas these obstacles are not insurmountable, they should nonetheless be appraised at their true value. In order to overcome them, there is probably a choice to be made in the priority of establishment which would produce the conditions necessary for these very elaborate developments. The participation of an experienced company, which it is useful to solicit for some of these productions, cannot be obtained unless one or both of the following conditions are fulfilled:

Possibility of entering a new market and thus increasing the volume of sales without competing with its own market,

Obtaining a finished product at a price which is such that it can accede to the new marker by being able, if the situation were to call for it, to adopt competitive prices.

On the other hand, the production of intermediate products, which are well defined chemical products, does not depend an such strict technical and economic limitations, and the participation of a foreign company, if it is capable to helping improve the market of the plant, is not of such importance.

# III.1.5. PROBLEMS OF UNIT SIZE

We saw in chapter I that investments do not vary proportionally to the unit output, but rather according to a power factor generally between 0.60 and 0.85.

Operational expenses and overhead are considerably reduced when the unit capacity increases. When allowing for the construction of installations with larger and larger capacities so as to be able to produce for export, developing countries must in particular take this factor into account if they are to be competitive.

# III.2. LIMITATIONS IN THE ACHIEVEMENTS OF A PETROCHEMICAL INDUSTRY -- MEANS OF REMEDYING THEM

# III.2.1. LIMITATIONS AND DIFFICULTIES IN ESTAE ISHING A PETROCHEMICAL INDUSTRY

These are generally imposed by :

(a) A relatively small local market and reduced export possibilities which do not warrant construction of industrial units with sufficient economic capacity and which make for extremely high production costs.

(b) Exchange currency deficits in cases where the domestic market or export perspectives are sufficiently attractive to enable installations to be built which entail large investments.

(c) The availability of raw materials.

Some means are not economically feasible. For example, whereas it may be possible to set up nitrogenous fertilizer production from natural gas under excellent conditions, it may also be extremely costly to envisage the production of plastics or synthetic rubber from the same sort of raw materials.

The multiplicity of by-products, which it is often difficult to valorize, is also an important element in the profitability of petrochemical installations using naphtha feed.

(d) The lack of experienced personnel in sufficient number to fill all the new jobs.

(e) The restricted growth of transformation industries and commercial circuits.

We have noted that developing countries can be in a good position compared with industrialized countries with regard to: cost of raw materials; transportation expenses; and the importance of certain local markets and the possibilities of exporting under certain conditions where sufficient quantities of products make it feasible to build installations of economically profitable size.

However, they can also find themselves handicapped compared with their more highly industrialized competitors in several decisive aspects such as: labour costs; construction costs; lack of exchange currency; and the limitations of certain markets and, consequently, the impossibility of producing at competitive production prices.

III.2.2. MEANS LIABLE TO REMEDY THE DIPPICULTES INVOLVED IN ESTABLISHING A PETROCHEMICAL INDUSTRY

The different fields of activity where special efforts should be made in order to remedy the difficulties specified above will be dealt with successively hereunder.

# 111.2.2.A. The labour force

It has already been mentioned that it is mainly the scarcity of highly qualified personnel which raises the cost of the labour force. It is thus necessary, if a petrochemical industry is to be developed in a country, to plan on a programme which will facilitate the training of the personnel capable of alleviating this situation in the long run.

The assistance of the educational institutions of industrialized countries is useful, at least in the beginning, in training engineers and technicians capable of personally taking a hand, as soon as they get back, in finding solutions to specific problems raised by the new industry established in their country.

The institutions necessary to provide for the knowledge acquired by these men must, however, be set up on the spot and as soon as possible in order to bring about a better productivity of the industrial investments which will ensue.

The co-operation of engineering and construction enterprise as well as process owners should be sought after, and the participation of competent foreign companies or organizations is also a lavourable way for a country to acquire rapidly the basic level of modern knowledge to work and to prepare to broaden and increase this knowledge. Care should be taken, however, to see that local cadres actually share in the responsibilities and that they are closely involved in the development of the new industry created in the midst of this sort of collaboration.

# III.2.2.B. Supplying investments and reimbursing exchange currency

Supplying investments and, more specially, exchange currency (which represents about 80 per cent of the investment burden can be done in two ways.

# III.2.2.B.a. The contribution of equipment credits and loans

These are essential instruments in furthering development. However, even though they spread out the investment burden over a length of time, they do not eliminate it and they are necessarily accompanied by a considerable increase in the absolute value of this burden which must support all financial expenses. Circumstances which are also due to the fact that the payments are deferred considerably increase the expenses involved in setting up a new installation (cf. Chapter II.1.4.B.). These credits and loans cannot alone and unconditionally solve the problem of the development of a petrochemical industry.

# III.2.2.B.b. Contributions by having foreign companies participate in the capital

This is a particularly desirable form of aid to development provided that the contributions do not conflict with the political structures that the country in question is freely adopting; and the forms assumed by this aid respect the following essential aims: meeting the actual needs of the aided country; and contributing to a task which in itself contains the conditions necessary for its ultimate spontaneous development.

The financial participation which is offered should thus be studied favourably from the following aspects and in immediate and future perspectives: contributions to financing the investments; guarantees concerning the planning of implantations and the managing of the project; current and future technical contributions; supply source and market contributions; and contributing to the speed of implantation.

Reimbursing exchange currency invested in the construction of a petrochemical complex should come from the exploitation of this complex which will provide: the resources needed to reimburse the invested capital in a reasonable length of time in the case of private capital and according to a set schedule in the case of equipment loans or credits; and a large part of the resources also needed to enable the new implantations to develop.

This reimbursement will in most cases, therefore, be made in local currency. However, the reconstitution of the "Invested Capital", at least in so far as the irrevocable payments connected with the credits go (cf. III.2.2.B.a), or the repatriation of profits associated with contributions of capital (cf. III.2.2.B.b) will have to be made in exchange currency. We shall see further on (cf. III.2.2.C) how an industrial development can probably be set up which is not only based on the potential of the domestic market, but which will spread over and beyond this structure and diversify the outlets for its products.

However, it must be admitted that it is difficult at present to establish an industry on the possibility of exporting its products, which would bring in foreign currency, because: identical projects based on this sort of outlets are being developed in all countries; mass productions in particularly favourable locations at low prices are more and more frequently finding their way into the international market; and many units now operating below their nominal capacity can provide products at marginal prices.

If, therefore, the new enterprise does not itself establish new exchange currency resources, its country will then have to take the responsibility for the transfers which the enterprise will eventually entail.

In some favourable cases, if the country has available sources of exchange currency from exports of other products or from co-operative ventures, the exchange currency thus brought in can ideally be used to partially cover the suitably spread out expenses linked to a new enterprise for domestic expansion. Such a use of exchange currency can be helped along by the savings of exchange currency which the new enterprise will produce compared with the imports that the country would otherwise inevitably have to pay for.

For example, for a country which annually imports 50,000 tons of ammonia at \$70/T in order to manufacture nitrogenous fertilizer, this means that \$3,500,000 in exchange currency has to be paid out every year.

The cost of an ammonia production unit corresponding to this capacity (including financing) would come to about \$11,000,000.

Assuming the following financing conditions:

- The total cost of the installations payable in foreign exchange currency is \$8,800,000, or about 80 per cent of the total investment;
- The loan obtained for this sum is repayable in 7 years with a decreasing rate of interest of 8 per cent, with a constant annual repayment of 19 per cent of the total in foreign exchange currency;

an annual payment over 7 years in exchange currency should be:

\$8,300,000 × 19/100 = \$1,670,000

In this manner there would be a saving in exchange currency of:

\$3,500,000 --- \$1,670,000 == \$1,830,000

which would enable the cost of the installations payable in exchange currency to be reimbursed in:

# \$8,800,000/\$1,830,000 - 4.8 years

In any case, taking into account the necessity of planning for exchange currency subsidies to enable petrochemical units to be established in developing countries, it is of the utmost importance that any development enterprise have recourse to only the strict basic investment minimum and that the share of this investment to be covered by foreign exchange currency in itself be reduced to the smallest possible fraction.

# III.2.2.C. Local market outlets and export possibilities

Choosing the production capacity of a planned installation should be based on the fact that at least 50 to 60 per cent of the nominal capacity will have assured outlets:

- On the local market (taking into account possible forms of protection in the form of customs duties on imported products);
- For export, by means of long-term contracts or exchange contracts between governments.

This raises many problems concerning:

# III.2.2.C.a. The local market

When this market is too restricted to allow for the construction of an economically profitable unit, production can never be envisaged at suitable costs despite the advantages which can stem from the low cost of raw materials and a favourable policy encouraging new investments.

# III.2.2.C.b. Export markets

We have already seen that prudence should be exercised in considering the development of a petrochemical industry on the basis of export markets. The constantly increasing competition from producers operating under extremely favourable conditions results in the lowering of international prices for which it is difficult to set highs or lows.

Furthermore, aid programmes in developing countries rarely have recourse to the possibilities offered by international trade, meaning that each country is led to manufacture an entire range of products by itself, thus automatically putting itself in a position of competing with neighbouring countries.

It can be expected, however, that regional economic unions will begin to be formed in the near future, thus leading to the opening up of very large markets and, consequently, the starting up of units with large production capacities.

In addition, certain foreign co-operative ventures can sometimes be accompanied by the opening up of a guaranteed foreign market, in which case they should be looked upon with particular favour.

The regional distribution of production units accompanied from the very beginning by trade agreements acts as a mutual guarantee of supply and enables each production unit to adopt the most favourable technical and economic conditions, and implantations to be undertaken which would not be possible if each country wanted to set up production of the entire range of products.

The technical and economic dispositions as well as the decisions which have to be taken to get together the means necessary for the development of petrochemical implantations are studied hereunder.

# III.2.2.D. The contribution of economic surveys and comprehensive development planning

Each implantation influencing economic and social development must be studied seriously to see to what extent the project meets the technical and economic conditions expounded above (cf. II.3 and 4, III.2.2.B). It can then be seen that an individual project cannot be certain of meeting these conditions unless it is enclosed within a well-studied comprehensive plan taking into account the additional implantations and installations located in the vicinity of the project and covering the supply of raw materials as well as the reception, transformation and distribution of finished products.

The aim of these studies is not only to co-ordinate the initiatives of the promoters (these initiatives must obviously be taken into consideration when they correspond to the different criteria enumerated above and when they form an integral part of the overall plan), but also to describe the technical and economic conditions which take into account: the foreseeable market for finished products and the transformation processes available, and which will make it possible to build industrial complexes which can better meet the criteria set forth in Chapter II. They will set forth an exact account of expenses and potential receipts. They will propose, if the case may be, various solutions which can be considered, with the advantages and inconveniences of each.

These studies, which must precede any decision involving the economic development of the country involved, are not very costly. They enable competent countries, which are inspired by generous sentiments but lack the large-scale means, to provide even despite this, countries so wishing with valuable assistance which can be a determining factor in their practical development.

These studies, which do not necessarily and inevitably lead to any particular sort of national or international, private or public structure, will, however, give all forms of co-operation the best possible chances of being found. This is why they should precede and not follow the invitation of financial assistance which will be necessary in any case to help make the industrial implantations possible.

In this manner, enterprises of all kinds will be much more easily invited to participate in the capital, due to the very fact that they will be well informed about the economic and technical conditions involved in establishing and operating all or part of the project in which they may be interested.

Furthermore, equipment credits or government-togovernment loans will be more easily obtainable for projects whose profitability and chances of success have been firmly established.

# III.2.2.E. Speed of establishment — "High Government Authority"

Once the plan has been drawn up, steps must be taken to see that it is carried through in the minimum length of time in keeping with other conditions listed hereunder.

This speed is necessary due to the fact that the validity of this kind of a project is in itself fairly brief (new production projects set up under very advantageous economic conditions; decrease in the prices of existing manufactures; modifications in the basic data taken into consideration in calculating the profitability of the project; appearance of new processes or of new products), and also because the decisions are all the more difficult to take and to follow through in that they usually imply the association of different ministerial departments.

It is thus recommended that a "High Government Authority" be created for each large-scale plan with each of the ministerial departments involved being represented.

# 111.2.2.F. Keeping control over the carrying out of a plan: "Specialized Technical Group"

The competent Technic I Ministry which will inform and submit to the "High Covernment Authority" the proposals to be decided upon and which will then be in charge of carrying out the decisions arrived at, must itself have a "Specialized Technical Group" constituted for the length of time needed to carry through the plan and responsible for: examining the policy decisions to be submitted to the "High Government Authority"; once decisions have been reached, examining the various possible solutions concerning the project; presenting the Minister at each step with the different options he has to choose from; and supervising and co-ordinating the activities of the different contractors selected until the entire project has been completed.

# III.2.2.G. Keeping investment costs down

One of the essential tasks of the "Specialized Technical Group" will be to take all steps necessary for maintaining investments at as low a level as possible.

We have already seen that this is the most important limiting factor in the development of an industry in developing countries (cf. II.1.4), therefore the following conditions will have to be respected in as much as is possible: efforts to save on investments must be considered as an essential element in the choice of processes and in the implantation of manufacturing units within the framework of carefully planned complexes; individual uchnical solutions bringing about reductions in initial implantation expenses must be sought after; any element causing these expenses to increase, such as: abnormal commercial relations; the temptation of sensationalism which could lead badly advised countries to place their prestige at the mercy of special techniques which are, in reality, inadapted to their problems; excessive political influences (even though some influences of this sort are perfectly legitimate and it is the purpose of the "High Government Authority" to enable them to be brought into play openly and efficaciously) must be avoided. In order to see that these conditions are respected, it will be necessary:

(a) To maintain operations in the following strict order, which already in itself largely excludes the intervention of unjustified price increasing factors:

Setting up contract specifications for each unit, drawn up by the "Specialized Technical Group";

- Selecting a limited but sufficient number of Engineering Companies to compete for the contract for carrying out each lot;
- Having each Engineering Company consult suppliers and having each of them compile, under their own responsibility, a "turn Key" bid which is reasonably indexed and accompanied, if necessary, by special conditions of financing;
- Critically examining the bids on the part of the "Specialized Technical Group";
- Selecting, by the competent Technical Minister or, on his proposal, by the "High Government Authority", the contractor to be awarded the responsibility of building and starting up the installations;
- Supervising the execution and turning over of the projects by, or under the control of, the "Specialized Technical Group";

(b) To give the first of these operations all the scope it needs.

Only contract specifications which are carefully conceived in all their details can provide maximum assurance that the choice will go to the contractor who will, in the long run, provide a ready-to-operate installation at the lowest cost.

The detailed drawing up of these contract specifications is a highly specialized and little practised activity. It requires that the project be studied very minutely, and it necessitates extensive consultations with process licensers envisaged.

As a result, sufficient time must be devoted to drawing them up, because well drawn up contract specifications facilitate the consultations by the Engineering Companies, enable them to submit their bids in a shorter length of time, facilitate the examination of the bids, and reduce the time that has to be devoted to this aspect of the project.

# 3. TECHNOLOGY AND OBSOLESCENCE IN THE PETROCHEMICAL INDUSTRIES FOR DEVELOPING COUNTRIES

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#### Preface

This paper is written primarily to illustrate certain ways by which the developing countries can go about establishing a petrochemical industry on a sound basis. Advice along these lines is already plentiful --- and some of it is, in our view, rather questionable. Accordingly, we feel that the nature of this paper and, more important, the subject that it encompasses, require that we set forth the question as to how a country can best go about building up a petrochemical industry geared toward the manufacture of its own most needed consumer products, and how far backward toward the raw materials the industry should be integrated. A corollary question relates to the selection of the products that should be initially manufactured, in line with the limited amount of funds generally available for financing such projects. This leads also to a consideration of the various technologies available for the manufacturing processes, which must be examined closely in terms of scale of production and the special conditions for the country undertaking this course. In particular, a very thorough knowledge of process trends and new technologies must be brought to bear on this problem; such knowledge is required even at the highest policy levels, involving technically trained policy-makers.

# Politico-oconomic impact on technical factors

There is no longer very much argument as to whether the developing nations should build a petrochemical industry. Almost every country starting on the road toward industrialization is giving serious attention to building up the manufacture of heavy chemicals and particularly petrochemicals so that the question really becomes when and how to get started. From the inception of the petrochemical industry in the United States through its adaptation and creative contributions thereto, particularly by The Federal Republic of Germany and the United Kingdom,<sup>1</sup> this industry has become, in the industrialized countries, one of the major growth industries, perhaps the most important of all. Hence, its applicability to less developed countries is surely of prime importance.

The scattering of new refineries will insure the ready availability of petrochemical raw materials for some of the developing countries. Thus, the Far East, Africa and Latin America, principally consuming areas, will begin to affect the international trade in chemicals as they become more industrialized. In Africa, the total crude oil capacity has doubled in 1964 (over 1963) and is expected to increase another 77 per cent by 1966. The 15 refineries that exist today will increase to about 27 in 1966.\* Of the 12 new refineries, nine are in countries which never before had any refining capacity. Although there is only one operating petrochemical plant at present, 12 plants are proposed, planned, or under construction in Algeria, Angola, Egypt, Libya, Morocco, Rhodesia, South Africa, Sudan and Tunisia. A similar picture exists in the Middle East, where refining capacity is expected to increase 12 per cent by 1966. In addition to existing petrochemical plants in Iran and Israel, current petrochemical projects include Iran, Iraq, Jordan, Kuwait, Lebanon, Saudi Arabia, Turkey and others.<sup>2</sup>

It is important to consider that the petrochemical industry generates further industrialization through the consumer products introduced - fertilizers, plastics, detergents, synthetic rubber and synthetic fibres. Internal manufacture of these products will not only meet present consumption, but provide for and make possible the anticipated increases in standard of living. A petrochemical industry, therefore, represents one of the early goals in the desired consumer-oriented economic planning. It is evident that, except in the most unusual circumstances, it is impossible to import for any length of time a substantial portion of those consumer products, since there is rarely enough foreign exchange available for such large-scale purchases. These reasons for the early establishment of such an industry are compelling enough to sweep aside a number of initially unfavourable economic aspects.

The establishment of a new petrochemical industry in a developing country must cope with many important problems. A partial list of these frequently includes most or all of the following: (1) lack of raw materials; (2) small domestic markets and low consumer purchasing power; (3) difficulties in breaking through on the foreign market; (4) low-priced competition from the industrially developed countries; (5) inadequate technical manpower and

<sup>&</sup>lt;sup>1</sup> This topic has been touched on in another paper by the author, "Growth of Chemical Processing in Western Europe and the U.S.A.", *World Petroleum*, August, 1962.

<sup>\*</sup> World Petroleum, April 1964.

<sup>\*</sup> World Petroleum, July 1964.

lack of skilled construction and operating labour; (6) little or no heavy industry to supply the sophisticated equipment and instrumentation required, and (7) lack of capital and, particularly, the foreign exchange component necessary to acquire the technology and the special equipment. These serious handicaps, among others, obviously present such formidable road-blocks to the establishment of a petrochemical industry that a tremendous challenge is created. Fortunately, there are a number of mitigating aspects so that, with good planning and a comprehensive knowledge of the economics and future technological trends, it is possible in many cases to proceed on a programme that can overcome or abate at least some of these problems. It is the objective of this article to discuss some rational approaches that may help the efforts of countries starting along this treacherous road. In presenting these viewpoints, it is recognized that the problems vary from country to country so that it is almost impossible to make broad generalizations. Partly for this reason, examples will he offered whenever possible in striving to present a logical approach to petrochemical planning --- based on present and future technology. It is further recognized that such viewpoints may not be universally accepted. Thus, each country must obviously judge for itself what aspects of this presentation, if any, apply in its case.

Let us now turn to certain advantageous factors present in many cases that tend to mitigate the adverse conditions listed above, and consider these factors in some detail.

# SIMPLER CONSUMER MARKET AND DEMANDS

The manufacturer in the industrialized country caters to a very demanding consumer. In the case of plastics, this leads to a multitude of formulations and a great spectrum of products. These conditions burden the manufacturer with higher investment, more storage facilities and working capital, and higher operating costs due to meeting the extreme specifications demanded ---sometimes with little justification - by the fabricator and thus the ultimate consumer. It is easy to see that a new manufacturer in a developing nation will - at least initially --- have an easier market to satisfy. For instance, a manufacturer of plastic dishes and cups may be able to restrict himself to a few colours of one grade of plastic material, such as polystyrene, and thus install a lowcost moulding plant that may soon build up enough capacity for a small, simplified polymerization plant. This method of starting with the manufacture of basic consumer products, and then integrating backwards into more capital-intensive production industries was used successfully in Europe, and is ideally suited to many developing nations.

Similarly, a polyethylene industry could be based primarily on supplying a general purpose resin for injection moulding of various containers and for making a heavy duty film for various types of bags. The demand for these two items alone — neither of which would have to satisfy the critical properties of transparency of most resins offered for sale in the United States and Western Europe — could bring about the construction of a single polyethylene train. Special refining facilities for making the various other resins would he added later.

# SPECIAL RAW MATERIAL SITUATIONS

Some countries are favoured with indigenous raw materials suitable for the production of petrochemicals. It seems obvious - but does not always follow - that these countries should stress the manufacture of petrochemicals derived from such materials. It is interesting to note, as pointed out in a United Nations report, Studies In Economics of Industry: Nitrogenous Fertilizers Based on Natural Gas,<sup>4</sup> that natural gas is still being flared in some developing countries. This valuable resource is an ideal raw material for several important petrochemical processes. Thus, an abundance of natural gas should lead to immediate consideration of ammonia and other nitrogenous fertilizers. Other possibilities might involve consideration of methanol, acetylene, trichlorethylene. While acetylene generally is losing out to ethylene as the raw material for the vinyls (the largest consumers of acetylene), it is not necessarily economic to import naphtha and crack it to make ethylene when acetylene can be produced from available natural gas. On the other hand, liquid ethane and propane may be present in sufficient amounts to permit economic extraction from natural gas; a cracker for production of ethylene and propylene can he built near the source of such liquid hydrocarbons, or near the point of consumption. If this is feasible, vinyl manufacture from ethylene obtained from cracking of such feedstocks may become more attractive than the acetylene route, and may swing the balance away from making acetylene at all, even from zero value methanes.

Low cost electricity is an important product of very cheap natural gas, and it can also lead in the direction of chlorine, since salt is almost always available from sea water, if not otherwise. Likewise, the availability of fermentation alcohols in large quantities at low cost can be the basis for numerous products. It is interesting to note that up to two years ago, Imperial Chemical Industries of Australia and New Zealand, Ltd. based its polyethylene manufacture exclusively on alcohol-based ethylene. Yet Australia is much further along the road toward becoming a full-fledged industrial nation than the countries now considered in the ranks of developing nations. Brazil is also operating an ethylene-from-alcohol plant and another is under construction in Pakistan.

Another typical situation is an excess of chlorine due to the relatively high requirements for caustic and soda ash. In one South American country, a project has just been authorized to use an entirely new process to make ethylene dichloride (for vinyl chloride) from by-product HCl, since no other use could be found for the HCl.

# HIGH SHIPPING COSTS FOR LOW-PRICED COMMODITIES

Although many misconceptions exist regarding the economics of shipping raw materials and intermediates, it is a fact that many high volume, low-cost products frequently cannot be landed in the developing nations

<sup>&</sup>lt;sup>4</sup> United Nations publication, Sales No.: 63. II. B.3.

at a price low enough to present serious competition to a proposed indigenous industry. We are witnessing today a tremendous, world-wide build up in fertilizer capacity largely because of this economic reality. The awakening interest in advanced agricultural methods based on synthetic fertilizers has provided the impetus for an almost explosive increase in demand, which may serve as a useful background for certain countries as yet modest petrochemical industry. In particular, the hydrogen and carbon monoxide (synthesis gas) available in every ammonia plant should be looked at most carefully as valuable feedstocks for other petrochemicals (e.g., oxo alcohols, toluene diisocyanate, etc.). On the other hand, where the raw materials for ammonia synthesis are not available at low cost, it may be reasonable to import the ammonia in tankers and go on from there. Recent'y a trend has begun for certain less developed countries, (e.g., Kuwait, Trinidad and Tobago) to build large ammonia plants from low cost raw materials, which would permit shipment thereof over very long distances and yet land it at costs below what could be produced economically in the respective importing countries on a smaller scale.

# NATIONAL POLICY MAY BE DECISIVE

While the many existing problems could be used to slow down the establishment of a petrochemical industry, this does not usually happen. There is the recognition that it is inevitable that some petrochemicals manufacture will eventually commence and that it may be desirable to create the industry first and let the demand catch up. This method also permits the orderly and careful planning of an industry, and allows time for the proper groundwork to be laid and direction to be established. The move must be bolstered by a series of supporting steps, including adequate tariff policy, allocation of foreign reserves to purchase the needed raw materials, and similar measures. Although these measures can impose a strain on other parts of the economy, it is expected that, given time, the industries formed will generate income through exports and conserve funds usually applied to imports. But the justification for such action is not necessarily only the creation of markets but also the establishment and training of a cadre of technologists and administrators who can then act as a nucleus for further growth. Thus, such pragmatic reasons may also bulk large in the over-all consideration of when and how to procoed. Under these conditions, usual economic considerations such as payout and return-on-investment calculations so necessary to the industrialized nations may be quite out of place, except by the application of an entirely different set of ground rules, which go far beyond those governing investment decisions in the industrial nations and include such items as "increase in national income produced per unit of investment" and "social rate of return". The base question becomes the needs of the society.

# "SKIPPING" AN INDUSTRY TO FAVOUR DOMESTIC Advantages

Although the promise of plastics has long been known, the strides now being made in the application of the various plastic materials in replacing more traditional materials such as wood, paper, glass, aluminium, and steel are truly astounding. We may now be at the point where countries will start to consider a plastics industry as one of the basic foundations to build on, and may thus defer the installation of some of the other industries until a later time. Since hardwood is not always available and the capital investment for a glass, steel, paper, or aluminium industry is one or two orders of magnitude greater than for plastics, it is not surprising that developing nations are giving most serious attention to the latter. Trends in the use of polypropylene and PVC for pipe, PVC and polystyrene and glass-reinforced polyesters for building materiala, and polyethylene for bottles, other containers and heavy duty bags, are being followed extremely closely.

This is a good example of the use of new technology in a "leap-frogging" role. Japan has partly followed this path, and has created an extraordinary plastics and fibre industry, fully competitive with the world industries in these fields; and in some respects more advanced.

#### LABOUR --- INTENSIVE PRODUCTS

Although the preponderance of petrochemical manufacturing processes are capital-dependent, there are some products that are more labour-oriented than others. Most certainly, this includes plastics end-uses and, to a somewhat lesser extent, synthetic fibres. By their nature, the petrochemical process industries do not require much labour but what labour is required tends to concentrate towards the consumer product side rather than the preparation of raw and intermediate materials. Hong Kong may be cited as an area where the availability of low cost labour has resulted in a highly active plastics industry. For the raw material and intermediate industries, however, the labour requirements are so small as never to justify site or size selection solely for employment reasons.

# REGIONAL GROUPINGS AND TRADE ASSOCIATIA NS

The small size of markets and the problem of competing with the heavily industrialized countries has led to the formation of trade associations and this trend may become even more pronounced. By pooling several countries' markets and apportioning the manufacture of the individual countries' particular advantages in terms of rsw materials, energy sources, or trade patterns, it may be possible to realize a sufficient plant capacity to make a project viable. Thus, it is less necessary for each country to be self aufficient, and thus often compelled to build uneconomically small-sized units.

Of course, the association of a country with a major trade association may also impart certain inherent advantages in terms of market outlets and tariff protection. The proposed Turkish Petrochemical project was discussed along these lines in the 15 November 1963 issue of European Chemical News. In this case, the Turkish economy was to benefit due to its associate membership in the European Economic Community.

Oil-rich countries like Middle Bastern nations could specialize in large crackers and ship ethylene and propylene to other developing countries less endowed in raw materials, even those not in regional trade groups. A similar approach to ammonia manufacture has already heen mentioned. However, unless the countries seeking to export such chemicals have a sufficient market to purchase their customers' products in return, such achemes are obviously bound to result in creating as well as solving problems.

## IMPOBITION OF PROTECTIVE TARIFFS

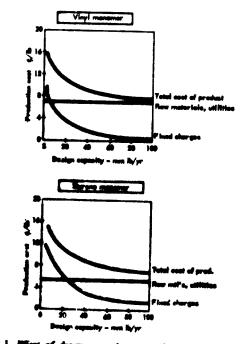
The need to protect a fledgling industry with adequate tariff is sine qua non but this policy must be regarded as a two-edged sword for it frequently results in two major dilemmas. First, it may raise the price level of the commodity in question and thus hurt not only the consumer but also the potential exporter of a product fabricated from the imported petrochemical. Again, in Australia, the tariff board allegedly encountered serious objections from plastic moulders when it recently raised the tariffs on polyethylene and polystyrene. By attempting to maintain resin prices at levels 50 per cent or more above United States prices, the cost of the fabricated products was raised to such levels that competition with the imported fabricated products became extremely difficult. This illustrates that in a free market economy various elements tend to influence such decisions, which are never easy. The second problem with high tariffs is, of course, their effect on the country's ability to trade with other nations and thus maintain a reasonable balance of payments. From these considerations, it just may not be feasible and would be foolhardy ever to set a tariff high enough to protect a very small, uneconomical plant. However, some tariff protection is obviously essential, as long as it is applied in the country's best over-all interest. This does not always happen, as is shown in the following example in connexicn with capital equipment. Mr. Frank G. Lamont, formerly Technical Manager of ICI (India), Private, Ltd., has pointed out (The Scientist (No. 326), 14 February 1963, Genesis of a Chemical Industry) that " The planner of a heavy chemical unit is, therefore, often faced with a prospective unit perhaps as small as one-fifth of the normally accepted se and cesting about twice as much per ton-year ause of the scale factor alone. Added to this, me of the equipment will be highly specialized and m be imported, involving packing, insurance, freight, etc., targes which may increase the capital cost by, say, a further 25 per cent. In the light of this, the levying of import duty on capital equipment is hard to understi

# TREBNOLOGICAL PACTORS

The precoding section has illustrated the interplay of economic factors which make up the background for the planning decisions. Such decisions may be strictly in the bands of government bodies or, in other enses, private industry. Programtly, as in India, government and private industry engage in joint planning studies, with the government in primery centrel particularly with sugard to extilug price irreds. In Japan, which estually developed in petrochemical indexts, makeh estually the last ten years, government planning, such as the approval of new projects by the Ministry of International Trade and Industry (MITI) has been carried out within a framework that is more closely based on commercial economic criteria and private financing. Japan's impressive progress in petrochemicals manufacture has been described recently.<sup>b</sup> However, regardless of the mechanism used for project approval, the key question remains: Is this a viable project, and how can the economics be improved?

The following list presents some of the most important criteria that should be considered in analysing the path a country is charting for its petrochemical development:

- (1) What are the most important products to start with?
- (2) Can the intermediates be imported? If not, should the raw materials be imported? This leads to a serious consideration of whether a cracker (naphtha or liquid hydrocarbons) is desirable for the initial installation.
- (3) Have all possible indigenous raw materials and other potential special advantages been considered?
- (4) What is the minimum economic size for (a) a vertically integrated plant and (b) an end product plant only?
- (5) Is the shipping cost for certain raw materials or intermediates less than the difference in manufacturing costs between the proposed high cost, small capacity plant and the giant installation in another country? Freight costs will rarely be more than 2-3 cents/lb. whereas the penalty for small plant scale may be far greater than that. (See figures 1 and 2.)



regard 1. apor of anoge expensive on production costs for plants menomers

<sup>&</sup>lt;sup>4</sup> R. Landso, T. P. Brown and G. S. Schaffel in Chemical and Replacemble Nove, 1 July 1968.

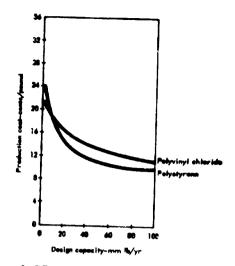


Figure 2. Effect of design capacity on production coasts for plastic polymers made from their basic raw materials

- (6) Can a packaged plant using standardized or otherwise modified design concepts result in better economics for a small installation?
- (7) Will products that instinctively appear a "must" on any list of proposed petrochemicals fit the country's present and future needs?
- (8) What processes and/or products are doomed to partial or complete obsolescence in the years ahead? Can a "leap-frogging" operation be carried out on the basis of new technology?
- (9) Has the list of proposed products and processes been reviewed by the most competent authorities in the field, or is it influenced by financial considerations which dictate the use of certain processes and/or equipment?
- (10) Has a given amount of money presumably available for the construction of petrochemical facilities been utilized to get the highest capacity of end products and the greatest increase in national income per unit of investment?

Consider the following example. A country desires to start a petrochemical industry based on polystyrene and polyvinyl chloride. Available are surplus chlorine --a situation fairly common in developing countries as mentioned above - and a small moulding industry that supplies a modest market of several thousand tons per year of PVC and somewhat less of polystyrene. This, then, is to serve as the backbone for a petrochemical complex. The plan is to erect a naphtha cracker to make the othylene raw material for the two plastics. It is recognized that the cracker cannot be built with a capacity of only 3,000-4,000 tons per year of ethylene, as required to supply the two monomer plants. Thus, a polyethylene plant is added to the complex to put the cracker into a more reasonable size range. Naphtha is to be obtained from a local refinery at reasonable cost and effectively without the use of foreign exchange. A realization of the fact that the large quantities of asphtha requi m

to make the sthylene gives rise to numerous potentially valuable additional petrochemical raw materials, leads to further additions to the complex. Butadiene is to be extracted and used for the manufacture of SBR rubber, thus increasing the capacity of the styrene plant to a more economic level. Propylene — which is inevitably co-produced at the rate of about 0.5 pounds or more per pound of ethylene — is to be used for the manufacture of tetramer and dodecyl benzene destined for detergents. The aromatic by-products, particularly benzene, are also separated. The cost of the complex is estimated at close to 50 million dollars. It will parallel similar installations set up in the 1950's in a number of the industrial countries and thus appears to be a well-conceived venture.

Now, what is wrong with this scheme? Perhaps a great deal. An initially modest plan to start a plastics intermediates industry, has mushroomed into a giant complex that may be impossible to finance, will make at least one product probably doomed to obsciescence and another of dubious importance. It may also exhibit prohibitive economics. In an attempt to justify a naphtha cracker, the planners have loaded the project with products that were never contemplated in the original plans and may help to scuttle the entire project. The naphtha cracker sized for very limited ethylene requirements cannot hope to produce raw materials at anywhere near world market prices. Including any reasonable return-on-investment, ethylene will be priced at 8 to 10 cents per pound, as compared to present world market prices of 4.5 to 6 cents per pound. (The influence of cupital on ethylene production cost is well illustrated in an article in the 10 May 1963 issue of European Chemical News. This discusses the trend toward crackers sized at 200,000 toms/year of ethylene.) In a vain attempt to justify an economical cracker, two future problems have also been created. Dodecylbenzene sulfonate-based detergents and SBR rubber may not at all be desirable for a new petrochemical industry. The former is not biologically degradable and is rapidly being phased out in the United States, Europe and elsewhere, by linear alkyl sulfonates and various non-ionic detergents based on primary and secondary alcohols. Styrene-butadiene rubber production is flattening out since the advent of stereo-specific rubbers such as polyisoprene and polybutadiene. Now, it may be quite reasonable to produce the more old-fashioned nonbiodegradable detergents and SBR to satisfy the local market. However, forward-looking planners would read the current technological trends to say that where there is still a choice, the newer products should be made. In this way, the developing country may actually gain an advantage over the industrialized countries by avoiding investment in anything but the latest technology. There is now also a growing realization that scape may still be the most important detergents in many developing nations and that syndets should be deferred at present.

Let us, therefore, go back to the initial objectives of this imaginary project which were polyvinyl chloride and polystysens. A careful and objective analysis of the economics may well show that the best course would be to delay the use of chlorine and to import vinyl chloride monomer and either styrens monomer (or stightenesse). Without prohibitive tariffs, both constantions could be

landed (including shipping and insurance costs) at well under 12 cents per pound - perhaps 10 cents for styrene and vinyl chloride, and less for ethylbenzene. These prices are easily 30-40 per cent under those calculated for the small cracker-based complex described above. these intermediates would supply new polymerization plants which can be erected with modest capital. Such plants should be reasonably large and should supply an expanded fabricating industry that is geared to the export trade, as well as to the supply of domestic demand. Having established a growing market, attention could then be paid towards promoting a market for other endproducts upon which the ultimate cracker could eventually be based. Naturally, as consumer demand and, hopefully, exports increase, it becomes more desirable to reduce the expenditure of foreign reserves for raw materials. The next step might then be to manufacture the monomers from imported liquefied ethylene. While this is not yet readily available as a market item, the advances in shipping liquid methane make refrigerated ethylene a sure thing of the future. This commodity may be available in ocean-going tankers at a cost not very different from world market prices. This is because incremental ethylene, made in locations where hydrocarbons are at fuel value or flared, can be priced at 3-4 cents per pound and shipping and handling charges should add no more than 11-2 cents per pound. Since in the case of both styrene (ethylbenzene) and vinyl chloride, the ethylene contributes well under 50 per cent of the molecular weight, the quantities of ethylene required for reasonable volumes of polystyrene and PVC are not enormous. This is just the reason why it is difficult to get naphtha crackers up to an economic size level. By purchasing liquid ethylene, and reacting it with indigenous chlorine and benzene (from a steel or petroleum source) the second step is taken on the road toward building a viable complex, still without a naphtha cracker. Meanwhile, it may be decided to start importing isoprene monomer and building a polyisoprene plant with a view towards achieving an ultimately favourable balance of ethylene and propylene. New technological trends toward more flexible ratios of ethylene to propylene may also assist in achieving an over-all olefins consumption on a sufficiently large scale. Polyisoprene is the only true "all purpose" synthetic rubber. When polyethylens demand builds up to the point where a plant can be built, the naphtha cracker then becomes an economic reality.

In another approach to circumvent the time factor necessatily involved in the foregoing example, the government itself might consider the construction of a large maphtha cracker and aromatics plant as a stimulus to industry, even though it may operate at a loss for some years. The plants could be financed on a long term basis, and fully justified over the time period. Raw materials would then be available to several small producers, allowing them to maintain a competitive position that they could never have achieved with their own raw material plants.

Thus, it may be seen that the developing nations stuat always be vigilant to avoid the twin pitfalls of unscomomical plant scale and obsolescent products and technology. Obsolescence, as employed in this paper therefore,

applies in the broad sense to obsolescence of scale factor as well as that of product and process. Each year the minimum plant size on the world scale becomes larger; the rate may even be increasing. The scale factor involves the most careful study of each project in terms of the country's own situation. Obviously, in the more heavily industrialized nations, it is easier to arrive at minimum economic plant sizes. Japan has now recognized the fact that its early petrochemical efforts were on too small a plant scale. Projects now being authorized by M.I.T.I. are on a much larger scale, in some cases involving several companies at the same location. An indication of the unit capacities of plants currently under construction in the United States and Western Europe, and hence of the potential obsolescence of new small petrochemical plants in developing countries, is given below:

													Tons per year
Naphtha Cra	ci	er	• .										200,000 (Ethylene)
VINY CRIOTA	de												100,000
SALAUG WOR	OF	ne	г.										75,000-150,000
Ethyia - Oxi	ide	e/C	Ŋ	/CC	SI.	•			•				75,000,150,000
Ammonia .	·	·	•	·	·	•	•			•	•		100,000-300,000
Cyclohexane	·	·	٠	•	·	·	·		•				60,000
Isoprene	•	٠	•	·	•	٠	·	·				•	45,000
Polyethylene	·	·	·	·	٠	·	•		·	·			60,000
PVC	·	·	٠	·	·	·		•	•	•			25,000-50,000

Inspection of this table and comparison of these individual plant capacities with a developing country's entire market requirement, over the next ten years or more, for these chemicals must give pause for sobering thought. This situation is made even worse if the country proposes to construct a number of widely dispersed petrochemical complexes, each of minimum size, as has been recommended in certain cases (although poor and therefore expensive internal transportation may, in rare situations, justify such planning as the lesser of two evils).

To appreciate the effect of plant capacity on production cost and required selling price, it is necessary to analyse the individual elements that are included in these calculations. These elements, in their broadest form, include (1) raw materials costs, including catalysts (if any), (2) utilities and other services, (3) operating and maintenance labour supplies, (4) taxes, insurance, administrative charges, and other overheads, (5) depreciation and interest. Items (1) and (2) are frequently termed "Variable Charges" and items (3), (4) and (5) are called "Fixed Charges". Assuming raw materials and utilities are always available at a given price — which is not necessarily true as discussed below - labour and maintenance cost will generally remain relatively constant over a fairly wide range of capacity while the other fixed costs will bear a direct relation to plant investment. This investment is related to plant capacity by an exponent that may vary from the 0.45 to 0.8 power," depending on the process."

<sup>&</sup>lt;sup>4</sup> This relationship is frequently plotted on log-log paper.

<sup>&</sup>lt;sup>1</sup> It should be noted that on a graph showing production cost as a function of plant than, fixed charges par pound of product must interest as production separity gats down. Variable charges remain constant since they are, by definition, density related to production capacity.

These economic considerations lead to the following realities that must be faced when planning a petrochemical installation:

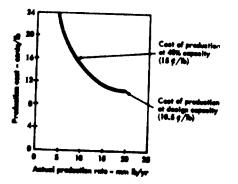
A small plant will be very heavily burdened by capital charges since the investment in terms of dollars per annual pound will be high. For most of the petrochemicals under consideration, the investment expressed in these terms is of the order of 5 to 15 cents per annual pound, for the large plants being built in the industrial nations. The lower part of this range would be representative of styrene or ethylene oxide; the upper part for polyethylene or TDJ. Since depreciation is frequently taken at 10 per cent per annum and taxes, insurance, overlieads, etc., can, in general be assumed as a function of capital investment, it turns out that capital-related cost-ofproduction items (excluding interest or capital-return) can usually be approximated at 20-25 per cent of the investment, i.e., 1-3 cents per annual pound, at full design capacity.

High tax burdens and capital return charges can be offset by various actions taken by governments to foster and support industrialization. Most common methods, now in use even in some of the more industrialized European nations, are high investment allowances, rapid tax write-offs on new investments, and highly favourable government loans with low interest rates.

However, the important effect of "fixed charges" on production cost at low capacities cannot be over-stressed. Figures 1 and 2 clearly indicate that for styrene and vinyl monomers and polymers, a penalty of 8-10 cents/lb. relative to plants of world market scale (higher end of graph) can easily result for undersized plants. While the absolute value of the cost data employed in these figures will vary, depending on the exact situation, the shape of the curves is quite general.

If a plant is operated at lower-than-design capacity, the fixed charges are spread over a smaller number of annual pounds. This has a particularly damaging effect on economics (see figure 3).

Up to now, only cost-of-production or "mill cost" as it is often called, has been considered. Since a return on investment or loan repayment and interest charges on borrowed cepital are usually required, a further penalty



region 3. Operation at expectitive lower share design (styresse). Design expective: 20 mm A/m

is imposed on a small plant operating at low capacity. By this time, capital charges may become unbea ably high. This is the reason why production costs in small plants frequently exceed those in large plants by far more than the shipping charges of the product that is to be manufactured.

Going back now to the assumption of constant raw materials prices, it is evident that if the raw material to Small Plant No. 2 is the product of preceding Small Plant No. 1, all the adverse factors discussed in Paragraphs 1 to 3 above come into play in raising the raw material "transfer" price to Plant No. 2. This is really the crux of the problem in building an undersized petrochemical complex.

The effect of capital charges on production costs in developing countries is well covered in *Industrialization* and *Productivity*, *Bulletin 5.*<sup>o</sup> In general, it becomes evident that small plant economics can become very unfavourable if care is not taken in selecting the economic size level. Although one would think that processes intrinsically exhibiting low capital investment ~ill be more adaptable to small economic plants, this may not necessarily be the case at all. This is because such processes also enable the industrial countries to put up huge plants for modest investments, which drops world market prices to the point where the much smaller plants in the developing countries find it just as hard to compete. Examples of this may be found in vinyl chloride, ethylene glycol, and cyclohexane.

Various approaches have been considered to arrive at smaller economically viable plants. These include:

(a) The use of standard or packaged plants, where the engineering component is greatly reduced and the complexity of the plant is sharply restricted.

(b) Examination of each section and piece of equipment to see whether it is economically justified in view of the abundance of labour and other factors in the developing nation. Certainly, such a plant should not be overinstrumented to save the cost of one or two operators. Batch vs. continuous operation could also be carefully scrutinized.

(c) Elimination of "gold-plated" construction standards that tend to be used in highly industrialized countries, especially in the United States. These have generally emanated from the petroleum industry, where continuous operation is paramount and plant cost is rarely a deciding factor. Such factors are frequently not applicable in quite the same way to petrochemicals manufacture. All standards adopted should reflect the latest developments in materials and equipment with prime consideration still being given to safety.

Incidentally, it may be well to mention at this point two approaches that are brought up from time to time but have not frequently been adopted. One of these is to construct a multi-purpose plant that can be operated in "campaign" operation to produce several products. This has been considered for various situations and is

<sup>&</sup>lt;sup>6</sup> United Nations, Industrialization and Productivity, Judictic No. 5, discusses the complex Susters that enter into the ordination of projects.

again being recommended strongly by an Indian Study Commission. Glycol ethers (for cellulose solvents and lacquers) and ethanolamines are today manufactured in campaign operation from ethylene oxide and various alcohols as are, of course, a variety of pharmaceuticals and dyestuffs. These latter cannot, however, be classed as petrochemicals. A possibility is a combined phthalic anhydride-maleic anhydride plant. These materials are in early demand in developing nations, the former as a raw material for plasticizers and paints, the latter for pharmaceuticals, insecticides, polyesters and other resins. The processes for phthalic anhydride and maleic anhydride based, respectively, on the oxidation of naphthalene or ortho-xylene and benzene, are superficially quite similar, being vapour-phase reactions followed by recovery and purification.

Another approach that has been attempted is to purchase a small plant made idle in an industrial country due to the advent of larger units. On the surface, this would appear to make sense for the developing nations because tariff protection and shipping cost could permit a cost-of-production penalty of 2-3 cents per pound versus the larger plant, which difference may have been enough to shut down the plant in the United States. (This case recently came up in connection with a vinyl acetate plant in the United States, which was to be dismantled and shipped to an Asian country). However, close study usually shows that saving the cost of the equipment is not worth the cost of dismantling and shipment when coupled with the fact that the plant is frequently based on obsolete or osbolescent technology.

When considering the processes to be used in the new undertaking, the need to maintain vigilance for obsolete technology and for processes that may lose their importance cannot be overstressed. We have already mentioned dodecylbenzene sulfonate detergents, although obsolescence in this case may not be an important factor in some developing areas. Major shifts in process technology are also occurring in the following:

Product	Older technique	New process
Vinyl chloride	Acetylene, largely based on calcium carbide	Ethylene-based, including oxychlorine- tion of HCl
Acrylonitrile	Acetylene plus HCN	Oxidation of propylene with ammonie
Detergent alcohols Acetic acid	Hydrolysis of fatty acids Ethanol oxidation via acetalde- hyda	Oxidation of straight-chain paraffins Direct ethylene oxidation or n-butane
Hydrogen (and ammo- nia/methanol)		oxidation Catalytic reforming of naphtha
"heno!	Sulphonation of Benzene	Cumene oxidation, dehydration of cyclohexanol, modified Raschig, and oridation of toking and
Caprolactam	Phenol via cyclohexanone	oxidation of toluene Several new technologies developing, such as photochemical, cyclohexane oxidation, and others
leinmine	From Dicyandiamide	From uren

Certain processes or products are frequently at a stage where it may be better to wait until the superiority of one technique or another has been clearly established. A partial list of such situations would include:

Pressa of product	lane
Polyester fibres	Should raw material be dimethy! terephthalale
Polypropylone	or pure terepithalic acid? Will this material have a future primarily as
Propylune Onide	a homopolymer or in supplymerization with, for instance, ethylene? The abserdaydrin process may become
Synthesis Babbar	unconcentral within a sheet period of time due to new technology becoming evaluate.
	The source synthesis robbase are reserving for more amphasis due to their greater ver- satility. Some SBR plants are partly being converted to polybuilding and ethylano- propyleme (SPT) robbar manufacture.

The utilization of new technology to gain special advantages may be illustrated with several other examples. A new oxo alcohol process recently developed makes butanol and 2-ethyl hexanol directly from propylene and synthesis gas (hydrogen and carbon monoxide). The latter can be made automatically available when an ammonia plant is installed—and at very attractive price levels when calculated on an incremental basis. The new ono technology can, therefore, point the way towards a simplified entry into the field of plasticiners, solvents, acids, etc. which in turn may lead to a favourable local export situation. A development scheme of this sort would lenging" over a fermentation alcohol-based derivatives setry, such as may be found in many sugar-rich countries of the world. A second example is afforded by the possibility of building a small, economically viable caproam plant. It is now anticipated that new routes un development will greatly reduce the size of economical sts and, for the first time, put one of the "miracle within the reach of most countries with a p ni indi nstry. It is, therefore, deemed desirable to

wait until the technology catches up with the need and makes the construction of a small, modern plant a reality. A third example is the case of building a cyclohexane derivatives complex to manufacture a number of important derivatives as satellite operations to a large oxidation plant. Thus phenol, aniline, cyclohexanol (for plasticizers) cyclohexanone (for caprolactam) and cyclohexylamine (for sweeteners and rubber additives) can be simultaneously produced in an integrated plant, and not by a number of unrelated processes, each of which individnally would be more expensive than in this new way of following the cyclohexane path.

# Major fields for industrial and consumer development

Is there an over-all master plan that should be followed in building up a petrochemical industry? The answer is probably negative. There are too many differences of a tangible and intangible sort. It is, nevertheless, useful to establish certain principles—as has been attempted above—and to make certain generalized recommendations. "Rather than approach the problem in either our country or less developed countries only from the development of knowledge and understanding, we must approach the problem from the needs of the society—agriculture, transportation, housing and construction, or whatever from the need end, if , ou will, rather than from the science end."

This is not a simple undertaking, but it is one that must be followed for the successful development of a new industry. Some of the considerations involved in such programmes are listed below:

### A. SYNTHETIC RUBBER

Synthetic rubber tyres are needed by all developing countries, mainly heavy duty tyres for trucks. Some countries have attempted to achieve a balance in the characteristics of available rubbers by building small polybutadiene and SBR plants while importing natural rubber, which is still essential for many uses, such as heavy duty tyres. Since practically all the desirable properties can be obtained from synthetic polyisoprene rubber, a less expensive approach would be to build only a polyisoprene plant, but this could then be of a size which is not uneconomic even by comparison with the major industrial countries. This restricts initial capital requirements, employs the newest technology, provides the single rubber generally considered the most versatile, and concentrates the entire rubber requirement in one large efficient plant instead of in several smaller and far less economic entities. Polyisoprene availability, furthermore, would make a country independent of natural rubber import, thus conserving currency reserves for other uses or imports. Then, too, the versatility of polyisoprene makes possible the manufacture of most consumer rubber products of high quality at low cost. Furthermore, it is based on propylene raw material,

\* H. Hellowon, "Modern Engineering and Society—the Marringo between Technical Ability and Sociel Need", Chemical and Engineering News, Jame 29, 1964. which is frequently available as a low-cost by-product from a naphtha or light hydrocarbon cracker and thus becomes a more attractive raw material than butadiene and styrene. Initial production could also be based on imported monomer.

The International Rubber Study Group, at its seventeenth meeting held in Tokyo in May, 1964, recognized that the normal market forces would not necessarily bring about a better balance between supply and demand for natural and synthetic rubber. In some countries (the developing nations) the saving of foreign exchange expenditure (for natural rubber) is a more important consideration than the absolute economics of synthetic rubber production in moderately sized plants. Furthermore, synthetic rubber capacity may be created for strategic reasons because of rubber's military implications. Lastly, while it may not always be economic in itself, it may be considered economic as part of a petrochemical complex.

This is a problem for natural rubber producing countries which are among the newly developing nations: Malaysia, Indonesia, Thailand, Ceylon, the Republic of Viet-Nam and Nigeria will produce an estimated 89 per cent of the world's rubber in 1964. Efforts are being made by the natural rubber producing countries, with the co-operation of the developed countries to diversify and industrialize their national economics with a view to lessening their dependence on natural rubber. The economic and political factors involved in the rubber, and more generally, raw material and commodity areas are so complex that they cannot be treated in a limited paper like this one.

# B. SYNTHETIC FIBRES

Rayon is rapidly being phased out as the most important synthetic fibre in the industrialized countries of the world. Its place is being taken by nylon. If a single fibre is to be selected by a developing nation's petrochemical industry, it should, undoubtedly, be nylon. Of the two major nylons (6 and 6/6), caprolactam-based Nylon 6 should be the choice. Nylon 6/6 technology is more complicated, since two materials, i.e., adipic acid and hexamethylene diamine are required to make the salt, and the capital investment for integrated Nylon 6/6 plants ia accordingly mugh higher. Thus, Nylon 6 production can be contemplated for smaller markets and with less technological risk, while still remaining economically competitive. Caprolactam and Nylon 6 spinning technologies are also easier to obtain under license. Caprolactam could initially be imported and later manufactured by one of the new processes.

Nylon is used in practically all branches of the textile and fibre industries from fine lingerie to industrial belting and carpeting. It has also become very important as a film and as a plastic resin. In the next few years, there is a strong possibility that mylon cord will even replace rayon in standard passenger car tyres. Replacement tyre sales are slowly moving in favour of mylon, and mylon is also making big inroads into the original equipment field for new truck tyres (in the USA). The increasing capacity of mylon in the developed areas reflects the present and future importance of this most versatile man-made fibre. Nylon uses extend to engineering plastics because of its special properties—high tensile and impact strength, stability at high temperatures, good abrasion resistance, and self-lubrication. Applications include its use as a substitute for metal in bearings, gears, cams, rollers, slides, door latches, and thread guides in textile machinery.

Polyester fibres require more technology and more capital, while the availability of know-how is much more limited. Manufacture of these fibres may therefore have to start, as it has in Argentina, Australia, India and elsewhere, by importing polymer and doing spinning locally. Acrylic fibres are least important in the (usually) warm developing countries and hence their manufacture (as well as of acrylonitrile) can well be postponed.

#### C. PLASTICS

The plastic to select is the polymer with the broadest range of properties and applications. This naturally suggests low-density polyethylene, which is used for injection and blow molding, film wire insulation, extrusion and other uses. The economics of polyethylene manufacture are such that when a market exists to take the output of one reaction "train", the cost-of-production from this train (excluding ethylene raw material) is not very much greater than for larger plants where several such "trains" are provided. The feedstock for the plant could be liquid ethylene delivered at low cost from a large cracker or by ocean tanker. As mentioned previously, general purpose polyethylene of a medium grade should be manufactured at first, with refining facilities deferred to a later stage to limit initial investments.

Polyvinyl chloride and/or polystyrene are next in importance, as consumption statistics usually indicate, and should soon be added to the complex. Again, only the polymerization plant may justifiably be built, based initially on imported monomers. It is interesting to note that in Western Europe polystyrene plants are being set up in various locations by two companies, supplied with monomer from large "mother" plants.

Melamine may yet become more important in the economy of developing countries, as it is now possible to make it economically from urea. The latter may be made on a large scale as part of a fertilizer complex being built in these countries. Under these circumstances, melamine plastic objects may take the place of other plastics which would be more difficult to make on a small scale.

#### D. FIRTILIZERS

Here the developing country may justify large plants because fertilizer is needed on such a large scale. Some oil companies are now embarked on a programme of installing ammonia, and in some cases urea and mixed fertilizer plants, adjacent to refineries. (cf. Chemical Week, October 26, 1963, The Fast East). In other cases, psckaged ammonia plants are available at low cost.

Ammonium sulphate plants will sometimes be added, although this material is decreasing in importance. More recently, ammonium nitrate, ures, and mined fortilizer plants are receiving considerable attention. Nitric acid may, therefore, also be produced in large quantities.

#### E. DETERGENTS

The trend towards biodegradable detergents will continue unabated, frequently regardless of the specific need. Australia is already considering the switch from dodecylbenzene sulphonate to the newer material even though there has not been a water table or stream contamination problem in that country. The consumer simply demands the latest product. Thus, alcohol-based detergents will be relied on more and more heavily. Where these can be produced from the hydrolysis of indigenous fatty esters such as coconut oil, this puts the country in a good position to produce the newer detergents. In other cases the trend will be to oxidize straightchain paraffins, available by molecular sieve extraction from kerosene streams in refineries, or by other new techniques.

# Two general examples-Spain and Mexico

It is interesting to look at a "still picture" of the Spanish economy in 1963 in terms of these considerations. Although Spain is not necessarily a typical developing nation, it only recently started to flex its petrochemical muscle. The table reproduced in the annex to this paper describes the output of the current heavy chemical and petrochemical industry, together with plans for the immediate future. The following points are worth noting:

(a) Polyethylene was 100 per cent imported at the rate of 15,600 tons in 1962, which led to the decision to install PE capacity, authorized in 1963/1964. Based on projected markets, three plants will be constructed with combined initial capacities of approximately 45,000 tons of low density polyethylene and 11,500 tons of high density polyethylene. Thus, the installation was held off until a large market was created.

(b) No dodecylbenzene production is planned even though an 8,000 ton market existed in 1962. A plant based on newer technology may be under consideration.

(c) Vinyl chloride is produced from low-priced chlorine that is quite out of balance with caustic soda production. Thus, an inexpensive raw material was responsible for an early plant.

(d) A tremendous expansion in fertilizers is under way, partly as a result of Standard Oil (N.J.)'s decision to participate in a complete fertilizer project at Malaga.

(e) The installation of naphtha crackers was deferred until the demand for polyethylene and such other large scale organic chemicals as ethylene oxide built up to the point where both the cracker and the ethylene users could be justified and then constructed simultaneously. The Tarragona cracker, which is fairly close to the economical projected petrochemical plants, including those of Dow Unquiness, will have a capacity of 74,000 metric tons per year of ethylene and 28,000 tons of propylene, which places it within the economical (word market) range. At Puertollamo, the Spanish state oil company, Calvo Sotelo, will install a naphtha cracker with a capacity of 71,000 tons of ethylene and 44,000 tons of propylene. Of course, Spain has no important supplies of light hydrocarbons or natural gas.

Turning to Mexico, the recent history of this country's petrochemical industry is described in detail and with great clarity in an article by C. O. Baptista of Petroleos Mexicanos, published in the June 1964 issue of *Chemical Engineering Progress*. An interesting guideline is offered as follows:

"As a generalization, one can say that if the total Mexican market, together with its calculated growth for the next three years, is as large as the capacity of the smallest economically operating plant in that line in the United States, the venture can be considered sound for the country and profitable for whoever may invest in it."

Among the important beneficial factors favouring Mexico are a stable currency, no limit in the foreign remittance of funds, extraordinary political "stability", and several others including government protection of markets (not cited). The opportunities offered by the Latin American Free Trade Association are also as discussed.

The policy of Pemex, the government-owned enterprise that operates the oil industry, is to build large plants and to make basic petrochemical building blocks available to other companies at reasonable prices. This policy is succeeding extremely well. Recent French financial assistance has further contributed to this development. In general, the co-operation between local and foreign investors has been excellent.

The types and sizes of plants constructed under this programme in Mexico are covered in the article, to which the reader is referred for details. Of importance in conmection with earlier remarks is the fact that Mexico chore nylon 6 fibre over all other synthetics and will soon proceed with a caprolactam plant. Also, that PVC and polystyrene have for a long period of time been produced from imported monomer.

# Availability of technology

All of these considerations assume that technology is always available when a country is ready to proceed with its plans. This is generally true, although there have been notable exceptions. The technology will either come from foreign manufacturing companies who are interested in cetablishing subsidiary operations in the developing nations, or from contractors licensing the processes for royalty and the opportunity to engineer and construct the plants. Rarely is the technology available in the country itself, during the initial phases; although process improvements will certainly be made locally as research, development, and chemical engineering activities are expanded. Japan, which licensed almost all its petrochemical technology (and this accounts to a large degree for the rapid growth of the Japanese chemical industry) is now starting to export the results of its new applied research and development in this field.

Licensing the technology does not necessarily protect the industry from gradual obsolescence. It is frequently desirable to arrange for information exchange agreements with the licensor, which provide for new developments to flow to the licensee as they are discovered. This is an important part of SD's ethylene oxide licensing. Thus annual technical meetings of licensees are held, with the company acting as a central clearing house for new developments, improvements, and techniques. Other companies have similar technological exchanges. A vigilant survey of the world petrochemical industry is also required, by following the numerous technical journals, attending such meetings as the World Petroleum Congress and ACHEMA, and forming a nucleus of enlightened chemical engineers who can affiliate themselves in a Chemical Engineering Society. This has occurred in many developing countries, notably India, Peru, Mexico, Uruguay and several others.

#### Conclusion

As can be seen from the contents of this paper, the problems in setting up a petrochemical industry for each development country are very sophisticated, requiring ultimate knowledge of technology, industry, trends, and economics. Seldom are all the skills necessary for such evaluations found in any one place, such as the private foreign manufacturing companies of the financial or governmental institutions which frequently include advice on the planning of petrochemical industries as part of the service they give their clients. Such advice needs to be supplemented and rounded out by expert technological counsel obtained from those actively engaged in the field who have intimate knowledge of the latest developments in the advanced industrial countries and who have as objective a view of the situation as may reasonably be attained.

#### ANNEX

SPAIN'S	NEW	BCONOMY
CALL MODIAL D		<b>ULUTION Y</b>

Product	1962 Production (austria sour)	1962 Jacquerte (mastrie tana)	Spanish Producers	Community
	188,880 (Dased on 188 per cont Ammonia)	1,870	9	1962 output increased 300 per east over the 1936 output
				Practically all of the achievants is used in fertiliner production in 1966 Ameniano Republic and Partiburts will have 300 matrio-ten-par-day units on stream at Makaga and La Carula

# ANNEX (continued)

SPAIN'S NEW BOONOMY (continued)

Produci	1962 Production (metric tone)	1962 Importa (metric loss)	Spanish Producers	Commit wis
BENZENE	(estimate)	1,020	5	
CARBON BLACK		13,300		Calatrava plans to build an 11,300 metric-tou-per-year plan at Santander
CHLORINE	44,500	97 <b></b>	ý	1962 output is 50 per cent higher than 1958 output Electro-Química de Flix (Spain's largest chlorine produce makes 44,000 metric tons chlorine per year at Tarragon
DODECYLBENZENE		8,500		terragon
HYDROCHLORIC ACID	26,785 Epaind on 100 per cent hydrochloric acid)		13	1962 output is 83 per cent higher than 1958 output
NITRIC ACED	94,000 (bscd ભા 100 per cent nicric acid)		18	1962 output is 77 per cent higher than 1958 output
<b>O</b>				Many fertilizer companies make nitric acid for captive use
Oxygen	29 million (cubic metern)		14	1962 output increased 260 per cent over the 1958 output
PHENOLIC REMENS.	3,500	267	16	1962 output is 20 per cent higher than 1958 output
POLYANIDES (NYLONS),	_	1,120		Used mainly for synthetic fibres
POLYETHYLENE		15,600		Dow-Unquinesa plans 20,000 metric-ton-per-year low density PE and 5,000 metric-ton-per-year high-density PI units at Tarragona Alcudia plans to make 29,000 metric tons per year low density PE at Puertollano Calatrava plans to make 5,750 metric tons per year high density PE, expanding to 11,500 metric tons per year a Puertollano
OLYPHOPYLENE	-			Dow-Unquinees plans an 8,000 metric-ton-per-year uni at Tarragona Paular plans a 7,000 metric-ton-per-year unit at Puertollanc
	6,999	2.000	3	1962 output increased 400
ULYUNITHANS.		44		1962 output increased 450 per cent over the 1958 output
OLYVINIL ACETATE	2,700	81	3	1967 support in 16 mer and bit to the second
ULYVINYL CHLORIDE	13,500	885	4	1962 output is 35 per cent higher than 1938 output 1962 output is double the 1938 output Etimo-Quánica plans to increase capacity at Monaón (Huesca) to 22,000 metris tors per year
UTANUM HYDRONDE .	2,000	30	3	1962 entput is 43 per cent higher than 1958 output
obium nyidingking:	154,669	8,700	7	1962 output equal to 1958 output Solvey at Terrulayeen has leavest connectiv (151 ero)
<b>TYNEM</b>				matric tone per year)
	1.3 million	6,400		Dow-Unquiness considering plans to make styrens
	based on 100 per cent adderic acid)	_	35	1962 output is 20 per cent higher than 1958 output Compañía Españosa de Mines de Río Tinto is building a 500,000 metrio-ton-per-year piant (based on 160 per cent sufferie acid) in Hustva province Many furilizer companies make sufferie acid for captive une
when a subsection a subsection of the subsection	-	1 <b>5,750</b>		Cointrova plana to make eis-polybutadious rubber (14,300 metris tems per year) and styrens-butadious rubber (13,600 metris tems per year) at Santander
	4,100 *	3,849	6	
	12,000	2,340		

Bernar: La Industria Quintes es Bunda 1985-predaction and import dats. Table reproduced from Chamberl and Busineering Hore,

· Mit Aguna.

# 4. RECENT TRENDS IN THE WORLD PETROCHEMICAL INDUSTRY

# F. N. Baumgartner and P. L. Richards, Marketing and Supply Department, Esso Chemical Company, New York

# THE WORLD CHEMICAL INDUSTRY

The chemical industry today is one of the world's most important industries. Over the past twenty years chemical production has increased more rapidly than any other large volume industry. Because chemical products affect almost every phase of modern life, they are essential to all industrially advanced nations. In fact, the more industrialized the nation, the more important is the role of chemical products. In the United States, for example, the chemical industry ranks fourth in the economy after petroleum refining, primary metals, and transportation equipment.

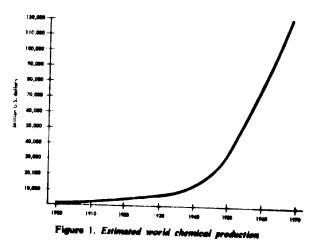
Before examining the world chemical and petrochemical industries, a few words about definition are in order. Today's variety of chemical products is so large, and the variety of chemical processes used by various industries so extensive, that it is becoming increasingly difficult to define the scope of the industry. No universally accepted definition exists today, despite the efforts of many experts. The method of recording national statistics often reflects the historical development of the chemical industry in a particular nation and bears little resemblance to data from other countries. It is thus virtually impossible to document the world chemical or petrochemical industries with any absolute consistency. To complicate matters further, the extent of accurate historical data varies widely from country to country. The analyst is thus faced with the problem of the chof; he must take apples, oranges, bananas, and other fruits of unknown quality and concoct a palatable compote.

The general statistical data presented in this paper are for the most part based on the definition of the cliemical industry as adopted by the Organization for Economic Co-operation and Development (OECD). Included in this definition are all chemical products classified under Section 5 of the Standard International Trade Classification (SITC), synthetic rubber (SITC Section 2, Sub-Division 231.2), and photographic supplies (SITC Section 8, Division 862). Excluded from the general statistics are synthetic fibres which are covered separately.

Despite these statistical difficulties, the available data do indicate trends, and it is our purpose here to examine a few of these trends as they may affect the developing nations.

During the early part of this contury, world chemical production grow at a very modest rate, reaching an estim-

ated value of \$10,000 million in the late 1930's. As illustrated in figure 1, production had reached \$50,000 million by 1955 and will probably exceed \$100,000 million by 1965. Eight countries account for three quarters of total production today as shown in table 1.



In 1950, the United States produced about 50 per cent of the world's total output, but the resurgence of the chemical industry in Europe and Japan has reduced this dominance to slightly under 40 per cent today. Among the 8 major producing countries, Japan is expected to

TABLE 1. THE WORLD'S LEADING CHEMICAL PRODUCING (Million US dollars)

·····	1938	1960	INI
United States of America	23,100	27,600	20.000
UNER	5,100		32,79
Federal Republic of Germany		7,000	9,000
Inited Wineday	4,060	5,400	5,900
United Kingdom	4,010	4,995	3.00
France.	2,595	3,485	4,360
haly.	2.071	3,350	1.94
<b>Aligen</b>	1,400	2,500	
Canada			- 1,100
		1,395	1,400
Personnage of world total.	70	75	

sevenine: CUCD reports; MITI chemical statistics; Deer chemical

undergo the greatest growth during the next decade. Some industry observers believe that before the end of this decade Japan will displace the Federal Republic of Germany; the third largest chemical producer behind the United States and the USSR.

It will be noted that the percentage of the total world market held by these eight countries has been increasing over the past few years. This indicates that although new chemical investment is increasing at a rapid rate in the developing nations, actual production is only now reaching a level high enough to reverse this trend.

Although comparative production data for 1963 are not yet available as this is written, an indication of chemical sales activity for this year is given in table 2 for selected countries.

TABLE 2. CHEMICAL SALES GROWTH IN 1963

-																-						Per conc 1963 vs 1962
United	Su	He	<b>.</b>																	_		e
Canada												•	·			•	·	•		•		,
Detted	<b>r</b> :		•	_	•	•			·	•		•	•	•	·	•	•	·	•	•	·	
U <b>nited</b>		-			:	÷	·	•	٠	٠	•	·	•	•	·	•	•	•	•	•		12
. 4941.91		γu	ΟĽ	<b>E</b> (		G	9 <b>F</b> 1	10	193	۱.												7
	· .																					ġ
taly .																		•		·	•	-
lelgium																			1	•	•	
main			•		•			•			·	·	•	•	٠	•	·	·	٠	•	•	
pain.	•••	•	·	•	٠	÷	·	·	٠	٠	•	•	•	•		•						11
<b>dexico</b>	• •	•		•																		15
apan																		-	Ċ	,	•	11
-								-	•		·	•	•	•	۰.	•	•	•	٠	•	٠	11

SOURCE: Chemical Week, January 25, 1964.

Of particular interest in this figure are the relatively large gains shown by Spain and Mexico. Chemical sales for 1963 for these two countries are reported to have been \$381 million and \$790 million respectively, and illustrate the growing trend for self-sufficiency among the developing nations.

# PETROLEUM BASED CHEMICALS

As the chemical industry has grown over the years, the demand for basic raw materials has exceeded what can readily be produced from coal and coking operations. The industry accordingly has turned to petroleum as a source of these materials and has attracted petroloum companies into what has been called the "petrochemical" industry. In general, in all industrial areas of the world, chemical raw materials based on petroleum and natural gas have exceeded the growth rate for the chemical industry as a whole. Although the first commercial chomical (isopropyl alcohol) based on petroleum was produced in 1918, the trend did not become significant until the early 1950's. Today organic chemical products wh and their origin in petro'vum and natural gas con ich a large share of the total market it ut tike te ni " has lost most of its earlier si articularly true when selecting to a n. It is unimportant in the market pi for enem ris, ortain ntes from pr o one he said for the w

chemical products on the market today. The classification "petrochemicals" has thus outlived its usefulness, and we, as well as other industry observers, advocate its discontinuance. "Basic organic chemicals" provides a more meaningful characterization of the primary organic building blocks upon which the industry is based. The classification includes only aliphatic and aromatic hydrocarbons, excluding quantities used as fuel, and allows statistical documentation to be accurate and consistent. The importance of raw material source, coal, oil, or vegetable, can be better appraised. The OECD has adopted this concept and the following remarks concerning chemicals based on petroleum have been largely drawn from this source.

The growing importance of petroleum as a raw material source for basic organic chemicals can perhaps best be illustrated by the trend in the Federal Republic of Germany, long a leader in chemical production from coal. Table 3 shows the change in the relative share of a few basic chemicals derived from petroleum from 1957 to 1962. Only benzene is still largely based on coal in contrast with the United States where approximately 70 per cent of benzene production comes from petroleum.

TABLE 3. RELATIVE SHARE OF BELIECTED BASIC ORGANIC CHEMICALS DERIVED FROM PETROLEUM -- FEDERAL REPUBLIC OF GERMANY

· • •••• · · · ·							-				-					1957	Per 4000 1960	1962
Methane.																		
A cost of an a		•			•	•		٠	•	·	·	•	٠	•	•	100	100	100
Acetylene	•	٠	•													28	33	42
Ethylene .																50	87	
lan same									•	•				•			•/	- 94
lenzene .				1			٠	٠								0	1	17
																15	22	
Cylene .															•			
			·		•	•	•	•	•	•	•		•		•	0	76	- 77

Production of basic organic chemicals in Western Europe reached almost 4.6 million metric tons in terms of carbon content in 1962 as shown in table 4. Oil and natural gas accounted for 58 per cent of this producon. In the United States 93 per cent, or slightly more than 12.0 million tons carbon content, was derived from oil and gas.

TABLE 4. PRODUCTION OF BARC ORGANIC CHINECALE

		Per 1000	electrol	from
	i,000 matrix satu amban suttiens	Off and Natural Gay	Caul	Other
Western Europe				
1961	4,016	54	43	1
1968	4,500			1
United States				•
1968	11,195	-	7	
1968	13,000		1	

Sevenes: COCD reports

The principle difference between the United States and Western Europe, however, is clearly illustrated in table 5. European production of aliphatic hydrocarbons is largely based on oil and natural gas whereas most aromatics are coal-based. In the United States, on the other hand, the aliphatic hydrocarbons are entirely oil-based, as are over four-fifths of the aromatic hydrocarbons.

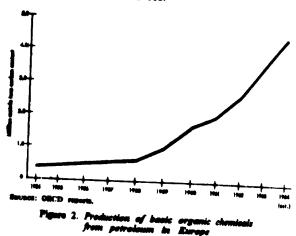
TABLE 5. PRODUCTION OF BABIC ORGANIC CHEMICALS IN 1962

		Per ci	mi obiained	from
	1,000 metric tons carbon content	Oil and Natural Gas	Coal	Other
Aromatic hydrocar- bons			nangenati - concert a ta recome	
Western Europe United States. Aliphatic hydrocar-	1,424 5,236	18 82	82 18	
bons Western Europe United States	2,844 7,803	<b>83</b> 100	15	2

Source: OECD reports.

The rapid growth in Europe of basic organic chemicals derived from petroleum is shown in figure 2. If the indicated trend continues, European production will have increased by 1,460 per cent over the decade 1954-1964.

Unfortunately, comparable data are currently unavailable for the USSR and Japan. Qualitative trends within these two countries, however, are consistent with the trends observed in Europe, leaving little doubt as to the dominating position oil and natural gas are attaining as chemical raw material sources.



Investments in chemical plants based on petroleum continue at a high level throughout the world. The value of new projects announced for 1964 has been estimated by the publication "World Petroleum" and is summarized in table 6. As expected, the largest share of the total investment, over 60 per cent, is accounted for by the large producing centres in Western Europe and North America. Asia and the Far East rank third, largely due to investments planed for India and Japan.

# TABLE 6, 1964 INVESTMINTS IN CHEMICAL PLANTS BASED ON PETROLEUM \*

	Number of New Projectz	Million U.S. dollars	Per cent
Western Europe	97	1,540	
North America	95	1,110 •	36 26
Asia and Far East	72	780	18
Africa and Middle East. South America	22	530	12
South America	25	342	8
Total	311	4,302 *	100

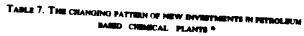
SOURCE: "World Petroleum" files.

· Excludes centrally planned economies.

Includes \$750 million for U.S.A.

· Actual World total estimated to be about \$5,400 million.

The investment pattern in petroleum based chemical plants has undergone a change during the past few years. In North America (principally the United States), the change from coal to petroleum as a raw material source has largely been completed. The development in Western Europe, however, is continuing at a rapid pace. Other areas of the world have only recently begun investment petroleum based chemical plants. The changing pattern in new investments is illustrated in table 7, which is based on announced investments for the years shown. Of particular interest is the large increase for Africa and the Middle East. Beyond 1964, we would expect the pattern to change sowewhat more slowly since limited local and available export markets for the developing areas of the world will probably preclude continuing large investments in petroleum based chemical plants.



(Percentage of world total)

	·													1961	1964
North Amorica.															
Western Europe		•••	•	•	•	•	•	•	•	·	٠	•	•	- 46	- 26
Western Europe Asia and Far Bast. Africa and Middle Ea	•	•	•	·	·	·	•	•	•	•	•	•		28	36
Africa and Middle He		•	•	·	٠	•	٠	•	•	•		-		15	18
Africa and Middle East South America		•	•	•	•	·	٠		·	٠				3	12
South America	• •	•	•	·	·	·	•	·	•	·	·	·		8	
														100	100

Encodes essivally planned encodering

# INTERNATIONAL TRADE IN CHEMICALS

A brief examination of the pattern of international trade in chemicals illustrates this point. Total experts of chemical products throughout the world have grown from over 96,000 million in 1959 to almost 96,000 million in 1962 (see table 8). Over one-half the total smart is

# TABLE 8. INTERNATIONAL TRADE IN CHEMICALS (Million dollars exported)

	1999 1960 2	61 1962
Western Europe	····· 3,750 4,256 4,66	M 4 440
	1 517 1 760 1 76	
	343 100 11	
Japan	167 169 11	
	····· 400 440 49	0 550
•	WORLD TOTAL . 6,077 + 6,804 + 7,24	12 + 7,735 +
Percentage of world production	···· <b>8.6 9.1 9</b>	.1 9.0

\* SITC, Section 5, " Chemicals "; United Nation Yearbook of International Trade Statistics. \* Minimum estimates.

attributable to Western Europe. Because of the EEC and TABLE 10. CHIMBCAL EXPORTS AS PER CENT OF TOTAL PRODUCTION EFTA trade groups in Europe, these data can be somewhat misleading. Table 9 presents a somewhat more realistic picture and indicates that over 90 per cent of the world chemical trade is conducted by the two European trade groups, United States-Canada and Japan.

TABLE 9. INTERNATIONAL TRADE IN CHIRDICALS -- 1962 -

						_								Addition U.S. dollars aspected	24
														2,308	34
Junior States		ad.	(	2		h	۰.							2.071	32
<b>PTA P</b>	•	•	•					•						1,391	21
<b></b>	•	•	•	•	•	•	•		•					262	4
Lost of world	۱.	٠		·	•	•	•	·	•	•	•	•	•	596	9
														6,530	100

· Derived from table 10.

\* Encludes trade within this group.

Although total chemical exports as a per cent of production are about 9 per cent, considerable variation entists among producing countries. As illustrated in table 10, the Pedersi Republic of Germany and the United Kingdom export about one-fourth of their production. This is partly a historical pattern but is also due to their association with the European trading groups. For , approximately 30 per coust of the experts of ral Republic of Germany are to BBC member trips and and ther 30 per count to oth wr We a countries. Roughly cas-b if of t he Usia il's esperts are de nd for 1 . It is easi D apparent, 1 **1** time of per W & 8 . nd countries. Con in. s is thus very inte 16. a Á 1

# FOR SELECTED COUNTRING

														-										H
Juited 1	l te	4-		•	Ås		-																	
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	•																							
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inited ]	Ki		4.	-										•	•	•	•	•	•	•	•	•	•	_
		-		-	•	•	•	•	•	•	•	•	٠	•	٠	•	٠	٠	٠	•	•	•	•	2
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and a									-	•	•	•	•	•	•	•	•	•	•	٠	•	•	•	
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anada	•	٠	•	•	•	٠	•					,												14
																				•	•	•	•	•
																10	1		D		_			

No discussion of chemicals anywhere in the world would be complete without some comment on prices. Although price is basically a function of manufacturing and selling costs which in turn are a function of scale of manufacture, the rule of supply and demand also enerts significant pressure on prices and, more importantly perhaps, on profits. The desire and willingness of chemical companies, petroleum companies and governments to participate heavily in the petroleum based chemicals field is resulting in over-production in practically all areas of the world. A highly competitive situation is developing with a corresponding decline in prices and profits. Table 11 shows a few examples of this decline in the United States.

TABLE 11. PN	ICE BECLINE	IN THE	Unimp	STATES.
--------------	-------------	--------	-------	---------

		1001	NA	
Banana #UBG	31	34	*	25
Aarylaalisiis (/ib	17	23	14.5	n
Philaile Anhydride (10.	17.5	2	15.5	12
Phonel (Mb. Conventional Polyethytane	16,5	17.5	14	ñ.s
	27.5	<b>37.5</b>	28-27.9	15-35

European prices have also been falling over the past 5 years and have reached a point where many chemicals now sell at or below United States prices. This trend has the obvious advantage of making larger volumes of materials available to more people at less cost. Competition will stimulate the more rapid adoption of new technologies and the manufacture of new products for the benefit of mankind. But the high profits historically associated with this industry will continue to decline.

The developing nations should pay particular attention to these trends, especially with regard to petroleum based chemicals. To be competitive and profitable, these products can only be produced in efficient large-scale facilities. Smaller, less developed countries desiring to build integrated petroleum based chemical complexes, buying relatively low cost petroleum feedstocks—if not available indigenously—must rely on export for most of their production. As shown in the preceding discussion, this export market is not only extremely price competitive, but, in fact, does not exist in a volume sufficient to let all of these countries be successful.

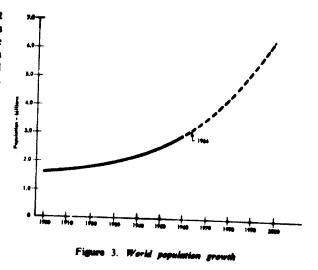
Obviously each nation must make its own appraisal of its own situation. Primary concern, however, should be directed toward obtaining the most economical raw materials. In many instances, importation of basic organic chemicals may be less costly than local production, even though indigenous oil or gas may be available. If this be the case, initial emphasis in developing a strong, sound chemical industry might best be placed on manufacture of chemical intermediates and consumer products. Investment in basic organic chemical production could await the time when local markets can support the necessary large-scale operations.

#### FRATILIZER

Having briefly examined the world chemical industry, let us now turn our attention to several sectors of the chemical business which have contributed significantly to the over-all growth. One sector which is of particular importance to the developing areas of the world is the fertilizer business.

World fertilizer consumption has been increasing steadily and will continue its upward trend in the future. The principal factor causing this trend is the increase in world population, which will double (over 1963) by the year 2000. With increases projected in nutritional and other standards, the demand for food and natural fibre production in the year 2000 will be even greater than the population increase alone would indicate. And with prospects visible for only modest increases in the land base available for agriculture, a large increase in agricultural productivity per land unit will clearly be necessary. This productivity increase will be accomplished by world-wide improvement in agricultural technology increased fortilization.

World population growth is shown graphically in figure 3. The shape of the curve indicates that not only is the population expanding but it is expanding at a continually increasing rate. Between 1920 and 1930,



for example, the increase was about 10 per cent. The decade 1990 to 2000, however, will see a 20 per cent increase.

The geographical distribution of population and the regional growth rates are even more significant than the total. As shown in table 12, two regions, Asia and Latin America, are growing faster than the other areas. The crucial population impact will occur in Asia.

# TABLE 12. DISTRIBUTION OF WORLD POPULATION

																		Share (per a		
	-																/969	1900	200	
orth /	<b>Lane</b>	rie	<b>R</b> .														7			
tin A	MM	100	۱.	•	•											·	ź		3	
	1.1	101	10														30		,	
		-				6		Α.									12	10		
	• •																Ĩ			
<b>.</b> .	•••	·	•	·	٠	·	٠	·	٠	·	٠	•	•				56	- 59	62	
	•••	•	·	·	•	·	·	٠	·	•	٠	·	·	•	•	•	1	1	- 1	
										W	ła:			-	-		100			

It would be misleading to imply that population alone is the ontice problem. If land resources were adequate, the population increase would represent not a problem but progress. That land resources are not adequate on he inferred from table 13. Asia, with over 60 per cont of the world's population in the year 2008, has today less than 30 per cost of the world's agricultural land. Purthermore, prospects seem poor for major increases in good land available for agricultural in the most pepulated Asian constitute. TABLE 13. DISTRIBUTION OF AGRICULTURAL LAND-1959

Regions	Age ( Thomas	Acres		
····	Croyland	Pasture	Total	capita
North America	0.6	0.7	1.3	6.6
Latin America	0.3	0.9	1.2	5.8
Western Europe	0.2	0.1	0.4	1.1
Eastern Europe and USSR	0.7	1.0	1.6	4 8
Africa	0.6	1.5	2.0	8.5
Neis a state a state a state a state	1.1	1.1	2.1	1.3
Doenia	0.1	11	1.2	75
TOTAL	3.5	6.4	9.8	3.4

The solution to the general problem will undoubtedly be a composite of many individual steps. Many of these will be directed towards increasing agricultural productivity. Increased fortilizer use will be one of the principal measures employed.

Two carefully prepared forecasts of fertilizer consumption have been published this year: one by Dr. Russell Coleman, President of the Sulphur Institute; the other by Dr. Frank Parker, formerly with FAO. These projections are shown on table 14.

TABLE 14. PROJECTED WORLD PERTILIZER REQUEREMENTS

(All data in million metric tone plant mutricut)

						 		_	 			 	1940	1979	1900
Parker .		,											27.7	53.3	<b>89</b> .7
Coleman.	·	•	•	•	·	·	•	•	•	•	,		28.1	46.5	

The two forecasts have a common methodologyboth being based on work done by FAO. The principal difference is that Parker's forecast is for requirements to achieve a minimum nutritional standard while Coleman's is for actual usage.

Looking at long range forecasts showing large increases in future total world fertilizer consumption is interesting but not very enlightening. A review of the present situation in fertilizers and a brief examination of the near future is more meaningful.

The recent history of world fertilizer consumption is presented in table 15. Total plant food consumption has shown a 5.2 per cent annual growth rate over the last 5 years. Nitrogen growth has been more than twice as

TABLE 15. WORLD PERTILIZER CONSUMPTION - HISTORY

Yours (onding June 30)	Consumption (militon metric tons)										
	N	P.O.	<b>K,</b> 0	Torai							
1957	7.3	8.2	7.1	22.7							
1958	7.9	8.5	7.4	23.8							
1959	8.7	9.1	7.9	25.7							
1960	9.1	9.6	8.2	27.0							
1961	10.2	9.8	8.5	28.5							
1962	10.8	10.0	8.5	29.3							
increase (over-all) Average annual	48 %	22 %	20 %	29 %							
increase	8.1 %	4.4 %	3.7 %	5.2 %							

fast as either phosphate or potash. Geographica! distribution of 1961/62 consumption is shown in table 16. Europe and North America are the largest consumers, accounting for 73 per cent of total plant food consumption. Asia and Latin America account for only 13 per cent of total communition. The ratios in which the plant foods are consumed are also of interest. For the world total the ratio is close to 1.3 - 1.2 - 1. There are, however, marked deviations from this in the regional patterns.

Turning attention to 1970, and limiting our remarks to nitrogen fortilizer and ammonia, the picture is shown in table 17. We expect 1970 nitrogen consumption to be about double the 1962 level. The important tonnage gains will be in Europe and North America but consumption in the under-developed areas will grow at faster rates.

TABLE	16.	Destautors	-	WURLD	PRYLIZER	CONSUMPTION,	1961/62
-------	-----	------------	---	-------	----------	--------------	---------

Jugine			Const (million a	natrie same)		Share of
······		N	**	5,0	Trust	intel
forth America		3.3	2.7	2.2	8.2	28 %
euth America		6.2	8.2	0.1	6.5	7%
	· • • •	4.4	4.4	4.6	13.3	45%
		8.9	6.5	6.7	2.4	1%
<b>Ma</b>		6.4	0.3	0.1	0.8	3%
<b>ele</b>		1.7	6.7	0.7	3.1	- ú%
lounia	• • • •	<b>0.1</b>	6.8	0.1	1.0	ЭX
	TUTHL	36.5	10.0	8.5	39.3	10×

TABLE 17. WORLD NITROBEN CONSUMPTION

Regions		( 100	Consumption Mon matric tog	w N)		inage Moreases
		1957	1962	1970	' <i>57</i> -'62	·6J- 7
forth America	• • • ·	2.2	3.3	7.0	8.5 %	9.5 5
outh America.	· · · ·	<b>9</b> .1	0.2	0.7	7.1 %	17.0
wope		3.0	4.4	7.0	7.5%	6.0
		0.6	0.9	2.0	9.3 %	11.4 9
frice		0.2	0.4	0.8	12.7 %	11.0
<b>ela</b>	• • •	1.2	1.7	4.4	7.5 %	12.7
vennia		0.1	0.1	0.1	4.6 %	10.4
	TOTAL	7.3	10.8	22.0	8.1 %	9.2 9

Although all three primary plant food elements are currently in short supply, the nitrogen shortage is perhaps the severest. This situation is expected to continue for at least the sext several years, although by 1970, newly installed nitrogen capacity should be able to meet the world demand. Local imbalances will occur, however, with North America having the largest over-abundance.

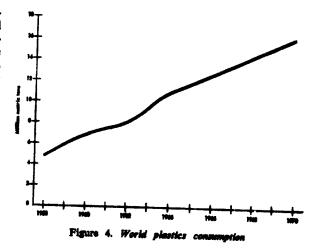
The significance of this situation to the petroleum based chemical industry is fairly obvious. Historically, ammonia manufacture has been carried out by chemical companies using coal as a raw material source, particularly in Europe. These companies have supplied the local requirements for nitrogenous fertilizers and have also oreated large export markets, especially to the developing areas of the world.

In the United States ammonia production was stimulated by the Second World War since nitrogen was needed for explosives. Various companies, including some petroloum compenies, were encouraged to build and operate plants for the government. After the war, these plants were sold to those companies who participated in the programme and they became the dominant producers. Since 1950, however, there has occurred a strong entry throughout the world by most petroleum companies into ammonia manufacture and ammonia derivatives for fertilizer. This is quite logical since ammonia manufacture meshes well with the petroleum business. Natural gas and refinery gas make excellent feedstocks, and a refinery has the flexibility of using almost any liquid product which may be available for ammonia manufacture. Equipment is also similar to facilities in refinery operation. Of perhaps greatest importance, refineries are distributed throughout the world and provide a manufacturing centre where ammonia is both needed and can be produced economically.

However, the trend toward producing ammonia in very large units in order to improve over-all economics, leads to the same problem mentioned earlier for hydrocarbons in that success depends upon finding large export markets if domestic outlets alone are insufficient. As more ammonia facilities are built throughout the world, exports as a per cent of production must decline. The actual volume of exports will probably remain high for some time in the fature, but it will be increasingly difficult to justify any large new investments in ammonia plants in the smaller developing nations. The trend rather will probably be for these nations to import ammonia for conversion to fertilizer in local mixing plants.

#### PLASTICS

One of the fastest growing sectors of the chemical industry is plastics, exceeding even the growth rate of basic organic chemicals in recent years. World production of plastics in 1963 reached a new high of almost 10 million metric tons. As shown in figure 4, production is expected to reach 16 million tons by 1970, representing a projected growth rate of about 7 per cent per year.



A breakdown of world production for several past years is presented in table 18.

In 1962, the United States accounted for 40 per cent of the total and Western Europe for 37 per cent, with Japan and Eastern Europe-USSR at about 9 per cent each. It is expected, however, that by 1970-3, the United States and Western European share will have declined to about 33 per cent for each area since the greatest growth is taking place in other areas of the world.

# TABLE 18. WORLD PRODUCTION OF PLASTIC MATERIALS (1,000 matric lans)

	1950	1960	1962	1962 per coni of world inte
United States.	2,042	2.830	3,540	40
	1,109	1,719	2.340	26
EFTA	533	714	950	Ĩ
USER and other Socialist				••
Republics	506	657	830	•
lapan	360	500	790	
Rest of world.	279	310	466	5
WORLD TOTAL	4,760	6,800	8,850	100

Sounce: Modern Plastics.

The world's leading producing contries are shown in table 19. The United States and the Federal Republic of Germany account for over one-half the total world production. In fact, almost 90 per cent of all plastics are produced in only seven countries.

TABLE	19.	MAJOR	PLASTICS	PRODUCERS
		(1	962)	

										 	~ .		*						i,000 matric im
United Sta	. ter	<b>,</b>																	3,540
LOCOLET N	opu	IOI	C (	Я	Ū.	C 1	ne	RУ											1.248
Japan .	•																		790
United Ki	n ge	lon	ħ.			,													745
Italy												÷	÷			·	·		500
USER.									Ż		·	·	Ċ	·		,	·	•	435
Fiance .				•			•						:	:	÷			:	420
																	л/		7,678
Per cent a	γÎ	nor	M	to	tai														87

SOURCE: Modern Plastics.

It is interesting to compare these data with per capita consumption and proportion of national income spent on plastics materials (table 20). As expected, the United States and the Federal Republic of Germany lead the world as plastic users with the United Kingdom, France, Italy, Japan and the USSR following in that order. However, the situation is quite different when considering the per cent of a nations' money which goes into plastica. Japan now leads the group followed closely by the Federal Republic of Germany and Italy. The United States and France lag far behind.

International trade in plastics amounts to more than 25 per cent of total world production as contrasted to the 9 per cent average for all chemical products.

The United States exports about 10 per cent of its production whereas the other major producing countries

# TABLE 20. PLASTICE CONSUMPTION AS RELATED TO POPULATION AND NATIONAL INCOME

(1962)

	Per septes communication	Bothmand he companyation per \$1,000 of national incom
Japan	77	21
Federal Republic of Germany	18.1	17
italy.	8.2	16
United Kingdom	11.8	10
France	9.1	1
United States	18.1	7
L'NGR	2.4	i

Sounce: Madern Plastics.

export 30 per cent or more. This international trade, however, is characterized by a large amount of movement especially between the European producers. Although the Federal Republic of Germany, the United Kingdom and Italy, for example, export 30-33 per cent of their total plastics production, they also import significant quantities. Net exports actually amount to about 20 per cent of production in these countries. Furthermore, if Western Europe is considered as an economic unit, then less than 10 per cent of its exports go outside that area.

Worldwide, the vinyl plastics lead in production is accounting for about 23 per cent of all plastics. The fastest growing major type of plastic, however, is the polyolefin category. This group at the moment amounts to about 20 per cent of the world total, mainly because of the early development of polyolefin technology in the United States Since 1958, production of polyolefins has exceeded that for the vinyl resins in the United States. In Europe, production is now almost two-thirds that for vinyls and is rapidly approaching a position of equal production. In Japan, vinyls still hold a commanding lead, but the general trend toward polyolefins is the same.

The advent of petroleum based chemicals has been largely responsible for this trend. During the early years of thermoplastics development, olefins from petroleum were relatively unavailable. Acetylene based on coal provided a ready source of vinyl monomers and led to the rapid development of vinyl resins. As petroleum began to replace coal as a raw material source, ethylene and propylene became available in large quantities. Emphasis shifted to the polyolefins, first in the United States and more recently in Europe, Japan and the world in general.

The longer range trend for polyolefin and vinyl resins is somewhat unclear with regard to the relative market position. Ethylene is also a raw material source for vinyl resin manufacture, and in many cases a more economical source than acetylene. Most new facilities for vinyl manufacture are being based on petroleum ethylene. Thus monomer source and availability will cease to influence the direction of the market. Instead each of these two leading plastics will find its market position on the basis of its ability to satisfy consumer product requirements.

Plastics have provided a logical entry into the chemical industry for many developing nations. Fabrication equipment is relatively inexpensive, and resins can be imported at attractive costs. The ratio of sales to capital is very high. Hence, small firms abound in the less developed nations. A number of these nations have already reached the point where demand is sufficient to justify resin production facilities, and these are being built.

Plastics are already firmly established in such consumer goods areas as housewares, appliances, and toys. The plastic packaging market, including bottles, is growing at a very rapid rate. Plastic pipe is beginning to make inroads on the metal pipe industry. Agriculture is also beginning to make use of plastics in such applications as mulch film, silo covers, and irrigation pipe. Considerable attention is being given to plastics for construction, particularly in areas of the world where other building materials are scarce. In short, we can expect plastics not only to continue to displace older conventional materials, but also to open new markets as yet unknown.

## SYNTHETIC RUDOKR

Another sector of the chemical industry which has contributed to its rapid growth is synthetic rubber. Synthetic rubbers are petroleum based and their growth has paralleled the growth of basic organic chemicals from petroleum. The 1940's saw the birth of the synthetic rubber industry because of the curtailment of natural rubber supplies as a result of the war. The industry received its greatest impetus in the United States. By 1946, synthetic rubber accounted for one-third of the total world rubber production as shown in table 21, and by 1962, production of synthetic rubber equalled that of natural rubber. This trend is expected to continue at least for several years, since natural rubber will be unable to keep up with the growing demand for rubber products.

TABLE 21. WORLD RUBBER PRODUCTION

(Per cent)

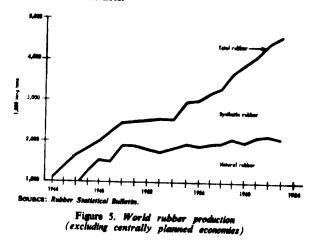
	1946	1952	1957	1962	1963	1964 est.
Natural	67	75	60	50	48	44
Synthetic	33	25	40	50	52	56

SOURCE: Rubber Statistical Bulletin.

In terms of total tonnage, natural rubber has been increasing very slowly. In recent years the industry has made technological advances in natural rubber production and it has been reported that yields as high as 3,000 pounds per acre have been achieved on a limited scale. It is unlikely, however, that these advances will materially affect the growth rate for natural rubber. Synthetic rubber should continue to fill the expansion in the market. These trends are illustrated in figure 5. World production of all rubber amounted to almost 4.5 million tons in 1963, of which 54 per cent was synthetic rubber. Slightly less than three-fourths of the latter production took place in the United States and Canada. As late as 1952, these two countries accounted for 95 per cent of all synthetic rubber production. During the last decade, however, the growth of the petroleum based chemical industry in Europe and Japan has seen a corresponding growth in the synthetic rubber industry. As basic organic chemicala from petroleum become available in other parts of the world, investment in synthetic rubber facilities will increase.

The recent development of the so-called "stereo" rubbers is having a significant effect on the entire rubber market. These synthetic rubbers are similar in many respects to natural rubber and consequently will compete most strongly against natural rubber. To a lesser extent, they are expected to make inroads into the SDR market because they seem particularly suited to the tyre rubber market which is the largest single outlet for rubber.

The entire future picture for rubber is further complicated by still another recent development. Synthetic rubbers based on ethylene and propylone are beginning to appear on the market. While outlets for these new polymers have not yet been fully developed, their remarkable characteristics assure them a sizeable share of total rubber markets.



Obviously, total rubber production throughout the world is dependent upon, and limited by, the consumer demand for rubber products. Rubber technology has been staying well ahead of this demand and new rubbers with new and unique properties are continually being developed. Each new rubber must, and will, find its niche in the total market. It is virtually impossible today to predict what the composition of the synthetic rubber market will be over the next ten years. About all that can be said with any degree of certainty is that the total market will continue to grow at a healthy rate, and that the older, established synthetic rubbers, particularly SBR, will probably lose position to the new rubbers.

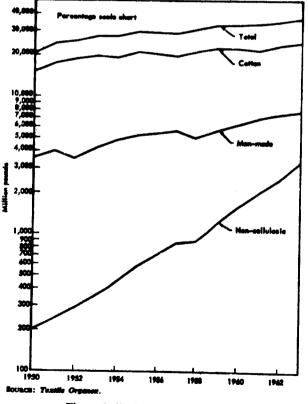
# SYNTHETIC FIBRES

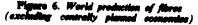
Although synthetic fibres have not been included in the general statistical data presented in this paper, no discussion of the world chemical industry would be complete without a few words about this industry Non-cellulosic fibres are becoming an increasingly important consumer of basic organic chemicals, even though their share of the industry is still relatively small.

World production of all fibres exceeded 37,000 million pounds in 1963, of which the man-made fibres constituted 26 per cent according to Textile Organon. The truly synthetic, non-cellulosic, fibres accounted for 2,936 million pounds or about 8 per cent of the total. Although cotton still dominates the market with well over one-half the total production, the synthetic non-cellulosics are experiencing the greatest growth rate, as shown in figure 6. This picture is similar to that for rubber in that the dominant fibre, cotton, is growing very slightly in total tonnage, but is losing ground to the man-made fibres as the total market expands.

Of the non-cellulosics, the nylon fibres lead in production with about 55 per cent of the total. The polyester and acrylic fibres follow in that order.

World production of non-cellulosic fibres by geographic area is shown for 1963 in table 22. North American production is mostly in the United States. In the European area, the Federal Republic of Germany, the United Kingdom, France and Italy are the major producers. Japan constitutes almost 97 per cent of the total shown for Africa and Asia, and in fact is second only to the





United States in synthetic fibre production. It is quite apparent that very little production is carried out in the developing areas of the world.

Although a number of the developing nations are beginning to invest in non-cellulosic fibre manufacturing facilities, this production will not be sufficient to alter the world picture over the next decade. Despite their outstanding properties, non-cellulosics are still more costly than natural fibres, particularly cotton. This is in contrast to plastics and rubbers where the synthetic product is often cheaper than alternate materials. Thus one can expect synthetic fibres to follow rather than parallel the development of other sectors of the chemical industry.

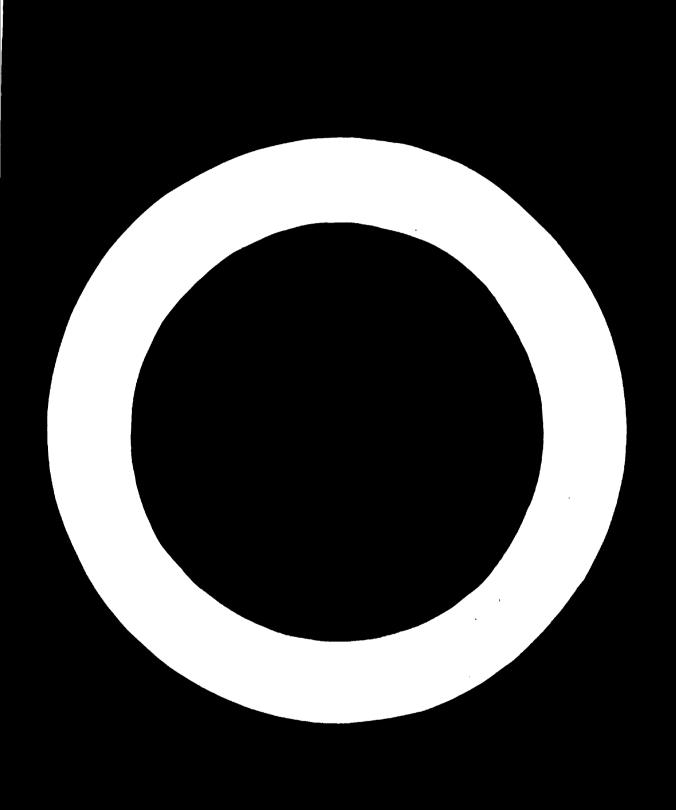
TABLE 22. WORLD PRODUCTION OF NON-CELLULORIC FIBRES

		•		 • • •		 			~		1963 / million pounds
North America											1,225
EEC											A60
Other Western Europ	•.						,				293
Africa and Asia .											543
Eastern Europe											176
South America		•	•		•	·					39
								Τα	<b>)T</b> /	AL.	2,936

Fertilizers, plastics, rubber and fibres are only a few of the sectors contributing to the growth of the world chemical industry. The foregoing discussion has of necessity only touched on a few highlights. Space does not permit inclusion of other sectors such as inorganics, pharmaceuticals, detergents, etc., but their influence is nonetheless important.

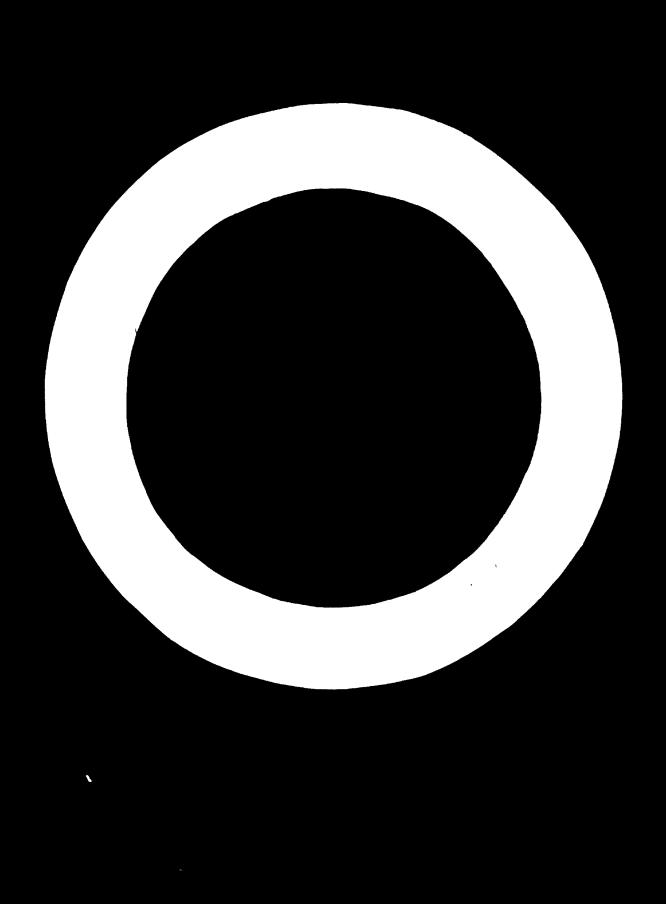
That the chemical industry is growing at a very rapid rate is self-evident. Petroleum has now replaced coal as the primary raw material source and will continue to increase its share of the basic organic chemical market. Overcapacity, low prices, and increasing labour costs, however, have reduced profit margins for these petroleum based chemicals. Competition in international trade has thus become very severe. The large and highly industrialized nations are in an excellent position to export. Although some smaller nations with sizeable local markets will install capacity for local production, they will find it difficult to compete on the export market with the larger nations. The successful development of the chemical industry in countries where domestic markets are relatively small seems most likely to come only through initial importation of low cost basic organic raw materials and local conversion to intermediates and finished products.

World-wide chemicals, and particularly those based on petroleum, offer excellent opportunities for investment. However, with the increasingly competitive nature of the industry, success will come only to those who can carry out their activities based on sound business principles and mature judgement.



Chapter 11

# ASPECTS OF DEMAND AND SUPPLY OF PETROCHEMICAL PRODUCTS



# INTRODUCTORY SUMMARY

In this chapter, the general conditions of production and consumption of petrochemical products are considered on the basis of the experience already gained by some countries or plans being made by others for the production of such major petrochemical products as plastics, synthetic fibres, synthetic rubber and nitrogenous fertilizers. There is, in fact, no doubt that the petrochemical industry has a great potential for accelerating the pace of industrial development. It has now been established that there are bright prospects for an increasing production of synthetics not only because of their efficiency as substitutes for the natural materials but also because of the high income-elasticity of demand for them. This means that with economic development, the demand for petrochemical products is most likely to increase.

The petrochemical industry is characterized by economies of scale and capitel-intensity of production. The larger the capacity output, the smaller the relative unitcost of production. Besides, the affinity of the various technological processes involved in the manufacturing process constitutes a cost-reducing element of considerable importance. In view of these economies of scale, the volume of demand or the extent of the market is a factor to be seriously taken into account in determining the appropriate scale of operation. In this respect, one might observe that the smallness of the market in most developing countries constitutes a veritable barrier to the prospects of taking any advantage of the economies of scale inherent in the petro-chemical industry. Developing countries might, therefore, consider regional economic integrations for the purposes of establishing those industries which perform better as large-scale undertakings.

In the international market, approximately 25 per cent of all the products bought and sold are classifiable as petrochemicals. But the problem of entering this market as a seller is essentially that of trying to enter a market which is already tacitly controlled by an oligopoly. The new entrant is obliged to negotiate some form of "gentlemen's agreement" with the established sellers or run the risk of being outcompeted carly in the encounter.

Leading producers of petrochemical products continue to be the major consumers thereof. North America and Western Europe, for example, account for the consumption of 70 per cent of the major petrochemical products. In particular, the United States of America and the Federal Republic of Germany are the largest consumers of plastic products.

The world's growth rate of the manufacture of plastics has been estimated at 13.3 per cent for the period between 1950 and 1964. The United States of America, the Federal Republic of Germany, France, Italy, Japan and the United Kingdom together account for 90 per cent of the total world output. Other European and centrally planned economies account for 9 per cent and developing countries like Brazil, Argentina, Mexico, India and China account for slightly less than 1 per cent. The incomeelasticity of demand for plastics is estimated at 1.7 per cent which means that the consumption of plastic products is significantly responsive to increases in per capita income.

The United States, Japan, United Kingdom, France and Italy account for 62 per cent of the world's output of synthetic fibres while developing countries, (Mexico, Argentina, Brazil, the United Arab Republic and India) account for 1.5 per cent. In consumption, advanced countries account for 85 per cent while developing countries account for only 4.5 per cent. Differences in income partly explain the difference in consumption rates — the income-elasticity of demand for synthetic fibres having been estimated at 1.4. On account of their greater durability and chemical resistance, synthetic fibres are increasingly serving as substitutes for the rest of the textiles fibres.

The other two major petrochemical end-use products are synthetic rubber and nitrogenous fertilizers. The world production of synthetic rubber caught up with and surpassed the production of natural rubber in 1962 and has increased steadily thereafter. The net-exporters of synthetic rubber include the United States of America, Canada, the Netherlands and Italy. Although the rate of preference of synthetic rubber to natural rubber has shown a steady increase, this does not mean that the market for natural rubber is shrinking dangerously In fact, natural rubber is still preferred to the synthetic: in the manufacture of heavy-service tyres.

In the last decade, the world production of nitrogeneus fertilizers grew at an average rate of 8 per cent per annum. The major fertilizers which are internationally marketed on a large scale are ammonium sulphate and ammonium nitrate. Western Europe and North America which are the major exporters account for 75 per cent of world output. The "density of use" (amount per hectare) of nitrogenous fertilizers is highest in Western Europe and lowest in developing countries. The productive use of fertilizers all over the world would appear to vary with the natural fertility of the soils on the one hand and the type of crops produced on the other. One would, however, expect an increasing use of nitrogenous fertilizers in developing countries whose economic mainstay is essentially agriculture.

In formulating a petrochemical project in a developing country, it is perhaps advisable to ask what tangible contribution to the basic needs (food, shelter and clothing) of the people might be expected of a petrochemical establishment. A question of this kind was asked in India and the answer was the assignment of top-priority to the development of petrochemical complexes.

The increasing scarcity of land in India for competitive uses has increased the need for the manufacture of *z* tificial fibres depending, of course, on the availability o. petroleum feedstocks. The choice of the type of petrochemical production to undertake should therefore depend, in the first instance, on the peculiar needs of the country and to a considerable extent on the local availability of raw materials like petroleum and natural gas,

For the appraisal of petrochemical projects it is not enough to have an idea of the present state of consumption, technical conditions of production and accurate cost estimates; it is also necessary to undertake an intensive market research in order to determine the extent of the probable market.

Is market research, the size of the total market, volume of experts and imports, competitive situation and future consumption are all investigated and quantified. A wealth of statistical data spanning a long period of time would, of course, be necessary for any reliable conclusion to be drawn. But in developing countries, the paucity of statistical data might constitute a handicap in making meaningful projections. In this case, s study of the experiences of developed petrochemicals-producing countries might prove helpful.

# 1. RECENT TRENDS IN PRODUCTION, CONSUMPTION, TRADE AND END-USES IN SELECTED PETROCHEMICAL PRODUCTS

United Nations Contre for Industrial Development

#### Introduction

This paper presents data, covering the period since 1950, on production, consumption, trade, and end-uses for plastics, synthetic fibres, synthetic rubber and nitrogenous fertilizers. In addition, it gives estimates by regions of potential future consumption for these products.

The data draw on a number of sources and, as such, are not strictly comparable. By and large, plastics are defined to include products of condensation, polycondensation and polyaddition (e.g. phenoplasts, aminoplasts, alkyds, polyallyl esters and other unsaturated polyesters, silicones); products of polymerization and copolymerization (e.g. polyethylene, polystyrene, polyvinyl, etc.); regenerated cellulose, and other artificial resins and plastic materials. With respect to synthetic fibres, they include polyamides comprising the various types of nylons; acrylics such as orlon, acrilan, courtella, leacril and cashmilon; polyesters that include primarily terylene; and polyvinyl fibres. Data referring to non-cellulosic fibres have been also used, which include besides the above synthetic fibres, other less important non-cellulosic fibres, such as glass fibres. Nitrogenous fertilizers exclude natural fertilizers and are given in this paper in equivalent of nitrogen content (N).

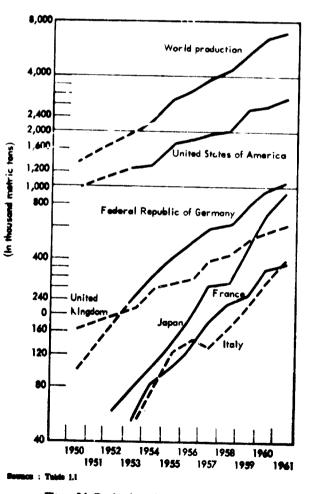
The data, when available, are given for selected countries as well as the various regions of the world; namely, Africa, Asia, North America, Latin America, the Middle East, western Europe and centrally planned countries. The Middle East is defined to include Cyprus, Lebanon, Jordan, Kuwait, Iraq, Iran, Israel, Saudi Arabia, Syria, the United Arab Republic and Yemen. Centrally planned countries exclude China (mainland) unless otherwise specified.

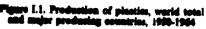
This study consists of four parts; part one covers plastics, part two synthetic fibres, part three synthetic rubber and part four nitrogenous fertilizers.

#### I. Plastics

#### PRODUCTION

1. World production of plastics has shown a steady growth, averaging an annual rate of 13.3 per cent for the period covered. The major preducing countries as indicated in table I.1 and figure I.1 are respectively the United States of America, the Federal Republic of Germany, Japan, the United Kingdom, France and Italy, sharing among themselves about 90 per cent of total world production. The United States and the United Kingdom have the lowest growth rates, 9 and 11 per cent respectively, among the six major producers of plastics, thus their share in total output has declined from 70 per cent to 40 per cent for the United States and from 12 per cent to 8 per cent for the United Kingdom for the years





# TARLE I.1. PRODUCTION OF PLASTICS AND NEWS OF INCOME AND MAJOR PRODUCING COUNTING, 1998-1943

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(In thousand metric has and provider)

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1950 and 1963. Japan and Italy scored the highest raves of growth, 25 and 23 per cent respectively, and their share in output has increased from 3 per cent to 14 per cent and from 2 per cent to 6 per cent respectively for the same period. The annual rate of production in France has been increasing at the rate of 20 per cent and the share in total output also increased from 2 per cent (1950) to 5 per cent (1963). The Federal Republic of Germany, on the other hand, has increased its production at the rapid rate of about 2/) per cent per annum and increased its share of production from 7 per cent in 1950 to 15 per cent (1963), becoming the second largest producer after the United States. The share of other European countries as well as that of the centrally planned economies has increased in world production.

2. A number of the developing countries, have undertaken the production of plastics; the major producing countries are Brazil, Argentina, Mexico, India, and China (Taiwan), sharing in the years 1958-1960 slightly less than one per cent of total output.

3. Tables I.2 and I.3 give data on plastics broken down into a number of important plastic products as well as into the major categories of thermo-plastics and thermosetting for the major producers for the period of 1955 to 1961. The data confirm the trend observed for a number of years, indicating a gain in the share of thermoplastics at the expense of thermosetting materials; such as phenolics and amino plastics. With respect to individual products, polyvinyl chloride and polyolefins have increased their share; whereas polystyrenes maintained their share of total output.

4. The production pattern in Europe and the United States of America differs; the share of thermoplastics is higher in the United States (72 percent) compared with Europe (55 per cent). The share of PVC is higher for Europe (21.4 per cent) than the United States (14.6 per cent); in contrast the share of polyolefins and polystyrene in the latter countries is higher than in Europe. This production pattern reflects differences in demand and supply conditions. For example polyethylene and PVC are good substitutes in a number of applications. Further, in the United States the fast growth of polyethylene has been associated with the highly advanced field of packaging which has not been the case in Europe. On the supply side, the relative abundance in the United States of ethylene either from natural gas or as a by-product of oil refining has been another factor contributing to the faster growth of polyethylene.

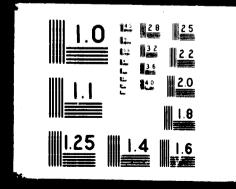
TABLE I.2. PERCENTAGE DETREBUTION OF VARIOUS PLASTIC PRODUCTS FOR MAJOR PRODUCING COUNTRIES, 1955-1961

		Thermosettings			Therm	plastics				
	Phonolics	Ures and molemies	Tetal	P.V.C.	Polyatyrene	Polyolefins	Total	Cellulose	Others	Tota
Total major produces				1	Percentages			n men kan in taun serien kan kan kan kan kan kan kan kan kan ka		
1955	13.0	8.7	39.9	15.2	8.3		54.1	4.8	1.2	100.
1 <b>956</b>	11.0	8.4	37.4	16.5	8.8		56.6	4.8	1.2	100.
1957	10.4	7.9	36.4	17.0	10.5		55.6	6.8	1.2	100.
1958	1 <b>0.7</b>	8.0	34.6	16.6	8.1		57.8	6.8	.8	100.
1959	10.2	7.5	31.7	17.3	8.2	15.9	59.5	5.9	2.9	100.0
1960	9.6	6.8	31.3	17.5	8.3	16.6	60.3	5.5		100.
1 <b>96</b> 1	8.9	7.0	29.7	17.6	8.2	18.2	63.1	5.3	.06	100.
ISA								5.5	.00	100.
1955	1 <b>2.0</b>	8.7	38.0	14.0	11.0	10.7	58.2	3.8		100.
1956	11.2	8.5	35.1	15.9	11.8	14.6	61.2	3.7		100.0
1957	10.0	8.0	33.7	15.7	14.7	16.1	62.9	3.4		100.0
1958	10.8	7.7	30.6	14.3	10.5	19.1	66.3	3.1		100.0
1 <b>959.</b>	11. <b>0</b>	7.5	28.1	13.9	11.0	21.0	69.1	2.8		100.0
1960	1 <b>0.6</b>	6.5	27.3	15.2	11.2	21.8	67.5	2.3	2.9	100.0
1 <b>961.</b>	9.9	6.6	25.7	14.6	11.1	23.9	72.1	2.2		100.0
hrope										
1955	14.8	8.7	43.2	17.2	4.0		47 4			
1956	12.0	8.3	40.9	17.5	4.3		47.4	6.5	2.9	100.0
1957	10.9	7.9	40.1	18.7	4.4		49.5	6.6	3.0	1 <b>00</b> .0
1958	10.6	8.4	39.5	19.1	5.0		45.6 46.9	11.6	2.7	100.0
1959	9.5	7.8	37.7	19.8	4.9	10.1		11.4	2.2	100.0
1960	8.8	7.4	36.7	20.6	5.2		49.7	10.2	2.4	100.0
1961	8.0	7.6	36.1	21.4	5.1	11.1	53.8	9.3	0.2	1 <b>00</b> .0
			30.1	41.4	2.1	12.3	54.9	8.8	0.2	100.0

Sounce: OBCD, The Chemical Industry, Pasia, 1955-62. United States Taciff Commission, Synthesic Organic Chemicals, 1958-62.

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	France	Japan	Italy	United Kingdom	United State
Thermosetting					
Phenolice Aminos	6.4 8.0	6.0	8.3	9.2	9.7
Alkyds Polyester	8.0	18.7 2.8	i1.8	13.2 8.9	6.4 7.8
Цроху		2.0		1.6	2.8
	14.9	0.2	9.0		1.0
SUB-TOTAL	(29.3)	(29.7)	(29.0)	(33.0)	<b>(27.7)</b>
Vinyl Styrenes	31.7 11.2	33.5	37.5	20.2	18.2
Polypropylene Polyethylene		3.0	9.8	8.6	16.6 1.4
Coumerone-indene	8.0	6.4 0.4	i4.0	21.0	23.3 2.2
Polyamides Others	7.2	0.1 0.1	6.0		4.1 0.8
SUB-TOTAL	(58.1)	(43.5)	(67.3)	6.3 (56.1)	3.5 (70.1)
Celhulosics	12.6	1.0 25.8	3.5 0.1	10.8	2.1
GRAND TOTAL	100.0	100.0	100.0	0.2 100.0	1 <b>00</b> .0

# TABLE 1.3. PRODUCTION PATTERN OF PLASTICS FOR MAJOR PRODUCERS, 1961 (Per cent distribution)

BOURCES: France and Italy — OECD, The Chemical Industry, Paris, 1961, 1962; Japan — John J. O'Con-nell, Japan Plastics and Resins Report, Noyes Development Corporation, 1963: United Kingdom — "Plastics in Great Britain", Modern Plastics, April 1963; United States of America — United States Tariff Commission, Synthetic Organic Chemicals and Stanford Research Institute, Chemical Economics Handbook.

# TRADE

5. Trade in plastics material and resin has been growing in the last decade at a faster rate than production, 20 per cent per annum and measured (export) in terms of total production; it increased from 11.5 per cent

to 20 per cent in the years 1953 and 1962 respectively. The six major producers (see table I.4) export about 85-90 per cent of the total. The United States of America, the Federal Republic of Germany and the United Kingdom are respectively the major exporters. The share of the United States ar the United Kingdom in total

TABLE 1.4. TRADE IN PLASTIC MATERIAL AND REBINS, MAJOR CONSUMING COUNTRIES, 1950-1964

(Metric tons)

	/930	1953	1955	1958			
					1960		1962
Europe		E	XPORT				
France Geraany (Fed. Rep. of) Italy United Kingdom Others BUD-TOTAL Japan United States of America.	1,300 n.a. 1,600 44,000 13,900 61,000 3,100 68,600 132,700	3,800 39,000 6,600 66,600 25,500 141,500 5,000 83,200 228,700	9,730 87,100 28,500 95,000 50,100 270,400 5,400 138,600 414,460	25,703 197,000 42,300 133,400 88,100 486,900 23,800 263,900	63, 100 263,000 100,000 186,300 166,400 781,810 50,901 324,300	76,100 390,500 134,300 220,600 189,500 1,013,000 53,500 480,500	80,392 365,000 169,150 247,434 236,635 1,125,001 82,852 499,403
		-		776,300	1,1 <b>56,680</b>	1,467,889	1,510,445

# TABLE 1.4. TRADE IN PLASTIC MATERIAL AND RESINS, MAJOR CONSUMING COUNTRIES, 1950-1964 (continued) (Metric tons)

	1930	1953	1955	19 <b>58</b>	1960	1961	1962
Europe		1 м	<b>IPOR</b> T				
France Germany (Fed. Rep. of) Italy United Kingdom Others. SUB-TOTAL	7,000 n.a. 4,800 12,700 28,700 53,200 10,500	16,200 8,500 6,800 11,600 51,800 94,900 31,300	22,200 18,800 12,200 29,400 107,700 190,300 11,600	42,500 61,000 23,500 43,600 209,300 379,900	56,400 104,800 53,000 97,700 380,800 692,700	76,500 111,300 68,700 75,800 491,100 823,400	100,76 135,00 56,350 103,58 587,716 983,41
United States of America	1,200	2,700	41,300	27,600 10,000	41,100 12,100	64,200 7.100	29,93
GRAND TOTAL	64,900	128,900	243,200	417,500	745,900	7,100 894,700	i 1,35 1,024,71

SOURCE: OECD, The Chemical Industry, Paris 1950-1963; Japan's foreign trade statistics year books.

# TABLE 1.5. TRADE IN PLASTICS AND REEN MATERIALS BY PRODUCTS, MAJOR COUNTRIES: 1960

(In tons)

	Prence	Per cent	Japan	Per cent	Itely	Per cent	United Kingdom	Per cenu	United States	Per cent	Total	Per ce
					Expor	T						
Styrenes	7.833	9.8	.179	.3	16.000							
Vinyls	37,942	47.7	26,543	.3 52.6	16,809	15.2	11,474	6.1	60,358	16.1	96,653	12.
Ures and Melamine .	1.760	2.2	.466	.9	58,857	53.4	97,364	52.2	34,587	9.2	265,293	31.9
Polyethylene.	1.518	1.9	1.186	2.3	10,277	9.3	19,967	10.7	10,348	2.8	42.518	5.
Cellulosics	14.401	18.1	.910		3,882	3.5	1.855	1.0	151,414	40.5	159,855	19.9
Phonolics	.544	.7	.129	1.8	3,128	2.8	18,027	9.7	27,906	7.5	64.372	8.0
Acrylics	.694	.,	.129	.2	1,904	1.7	16,120	8.6			18,697	2.3
Alkyds.				.1	1,462	1.3			8,225	2.2	10,440	1.3
Coumaronn-indene	.202		• •	• •	0.08	• •	5,719	3.1	17.206	4.6	22,933	2.9
Polyamides .	4.824		••	• •	0.28	• •			11,335	3.0	11.565	2.9 1.4
Others.	9,798			••	0.97	.1					4.921	
	3,130	12.3	21,047	41.8	13,839	12.5	15.982	8.6	52,904	14.1	113,570	·( 14.2
TOTAL	79,516	100.0	50,519	100.0	110,291	99.8	186,508	100.0	3 <b>74,28</b> 3	100.0	801,117	99.9
					IMPORT							
tyrenes	10,272	16.6	6,686	16.3	3.068							
inyls	10,917	17.7	.399	1.0		4.3	11,211	11.8	.229	.9	31.466	10.7
Irea and Melamine .	8,227	13.3			6,173	8.7	36,292	38.2	13,721	54.5	67,502	23.0
olyethylene	13,593	22.0	23.390	56.9	11,330	16.0				_	19,557	6.6
Siluicaica	4.299	6.9	1.249	3.0	9,451	13.3			.836	3.3	47,270	16.1
henolics	3,700	6.0	.850	2.1	7,693	10.9	5,182	5.4	6,948	27.6	25,371	8.6
orylice	1.751	2.8	.921		1,606	2.3	· · ·		1,842	7.3	1,000	2.7
lityds.		<b></b>		2.2	3,724	5.3					6,396	2.2
omnarone-indene	.836	1.3			2,010	2.8	2,955	5.1			4.965	1.7
stranides	2,956	4.8	<del>~</del> ·		2,002	2.8			.591	2.3	3,429	1.7
there .	5,368	8.5			.803	1.1	-				3,761	1.2
-		•	7,500	18.4	22,958	32.4	39,405	41.5	1,025	4.1	76,346	1.3 25.9
TOTAL	61,821	<b>99.9</b>	41,075	<b>99.9</b>	70,830	99.9	95,045	100.0	25,192		293,963	100.0

Bounce: Porsign trads statistics yearbooks of individual countries.

 
 TABLE I.6 NET TRADE IN PLASTICS, BY MAJOR PRODUCTS, 1960 (Export minus import in tons)

	France	Japan	lialy	United Kingdom	United States
Styrenes .	2,439	6,507	13,741	.263	60,129
Vinyls	27,025	26,144	52,684	61,072	20.866
Urea-Melamine	6,467	.466	- 1.053	+ 19.967	+ 10.348
Polyethylenes	12,075	22,204	- 5,569	+ 1.855	+ 150.578
Cellulosics	10,102	339	- 4.565	12.845	+ 20,958
Phenolics	3,156	721	.296	16,120	1.842
Acrylics	1,057	862	2.262		8,225
Alkyds			2.002	2.764	17.206
Coumaron	634		- 1.974		10.744
Polvamides	1.866				10,744
Others	4,530	13,467	9,129	- 23,423	51,879
TOTAL	17,695	9,444	39,461	91,463	349.091

SOURCE: Sec Table 1.5.

export declined from 36 per cent to 25 per cent, and from 27 per cent to 15 per cent in the years 1953 and 1962 respectively. The Federal Republic of Germany gained from 17 per cent to 23 per cent for the same period, surpassing the United Kingdom.

6. Western European countries, along with the United States and Japan, are the major importing countries, sharing about 60 per cent of total trade; the big six countries (United States, Federal Republic of Germany, United Kingdom, Japan, France and Italy) alone shared about 30 per cent.

7. The major types of plastics that enter into trade are given in table 1.5 for five big exporters. The table indicates that the most traded commodities are respectively vinyls, polyethylene, styrenes, cellulosics and urea melamine. The pattern of trade for each country reflects naturally the degree of specialization or diversification in local production. For example, the major plastic exported from the United States is polyethylene comprising about 41 per cent of the total, whereas in the exporting countries of Europe and Japan over 50 per cent of total export consisted of vinyls. On the import side, polyethylenes comprise the largest share of the total for Japan and France, whereas vinyls comprise the major items imported by the United States and the United Kingdom.

8. An analyses of net trade in plastics (export minus import) for the major producer indicates that in the past decade the United States, the Federal Republic of Germany and the United Kingdom were net exporters, whereas the remaining three have been, for a number of years, net importers, and only in recent years has their positon changed to that of net exporters. An analysis of net trade for individual products (see table 1.6) sheds further light on trade. Of the five countries only two, the United States and the United Kingdom are generally considered, and with varying degrees, net exporters in most plastics; the remaining three countries specialize in export of selected products and depend partly or fully for others on import. 9. Measured in terms of local production, the share of export for the major producers differs greatly, whereas for the Federal Republic of Germany, the Uniteo Kingdom and Italy the share of exports in recent years exceeded one-third of the local production; in France it had a share of about one-fourth, and the share was roughly 13 per cent and 8 per cent respectively for the United States and Japan. This share becomes greater for the major types of exported plastics, excluding Japan. The share ranged generally between a quarter to one-half of local production (see table 1.7).

10. Direction of trade in 1960 is given in table 8 and indicates a concentration of trade in the European and North American regions. Developing countries shared 20 per cent of the total export. The direction of trade indicates also regional specialization, thus Japan trades heavey with Asia and Oceania, and the United States with Canada and Latin America. Special trade patterns

TABLE I.7. EXPORT AS PERCENTAGE OF PRODUCTION, BY PRODUCTS, MAJOR EXPORTING COUNTRIES, 1960

Products	France	Japan	italy	United Kingdom	United States of Association
Phenolics.	2		7	27	_
Aminos	8		30	24	6
Alkyds				11	7
Vinyls	34	10	56	86	Ś.
Styrenes	18		44	23	12
Polyethylenc	4	3	10	1	25
Acrylics	•		14	1	
Coumaron-indene		-			- 14
Polymides					
Collulosics	10				
	38	11	24	27	42

Sounce: Calculations based on table I.5.

· Under 1 per cent.

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						Edokt	Ŀ							
		25	6,433 817	12.7	9,202 2012,9	2.7	4,869 2,071	2.6	62,226	16.6	5,489 2,000 2,000	5.5	90,055 210,055	6.1
	197-14	36	16,656	33.0	241,570	4.02	19,734	42.8	172,403	48.1 1	57,44	57.7	615,234	<b>3</b> . 19
	3,973	5.0	116.	1.8	18,325	5.3	905,9	5.1	.318		23,606	23.7	56,639	5.0
	Ē		6,112	12.1	105,9	1.9	12,334	6.6	13,225	3.5	69¥	0.5	38,648	3.4
	1	7	17,530	34.7	2.72	7.2	18,806	10.1	63,973	16.9	4,186		130,650	11.5
		<b>6</b> .1		1.0	9,073	2.6	<b>D.A</b> .		3,115	1.0	2,085	2.1	15,200	1.4
		6.1	547.	4	11,432	3.4	<b>D.A</b> .		8,804	23	1,512	1.5	24,039	2:2
Other countries	- 145 31	9.6	<b>8</b>	1.7	ł		59,166 b	31.7	4,821	1.2	1,873	1.8	83,063	7.3
Games TOTAL	79,516	100.0	<b>50,</b> 519	160.0	343,149	100.0	186,508	100.0	373,916	100.0	99,692	100.0	1,133,300	100.0
						Ineroen	F							
The Amin	21,529	36.6	33,62	<b>81.4</b>	31,753	30.5	44,714	45.4	2,244	20.0	16,996	28.2	150,958	40.4
	37,841	<b>7</b>	2.65	17.0	67,142 4,550	13 <b>4</b>	50,525 2,796	51.5	1.722	65.0	40,289 2 519	67.0 4 7	210,205	56.2 2 2
	.0 <b>4</b> 3		611	1.6	685	0.7	391	4.0			378	0.6	1,529	0.2
Gaune TOTAL	99766	100.0	41,025	100.0	104,130	100.0	98,426	100.0	11,3%	100.0	60,182	100.0	374,279	100.0
			2, 1940; Jap 2, 1940; United 1 and Italy: F.	an: Amu Kingdon Freign Tru	I Returns of Fo I Truste and No. de, Series C, 1	Fortin Nerige C. 1960.	• Includes		SAC TRUC	territories. territories.				

aside from regional specialization are also observed. The Federal Republic of Germany is the second leading exporter to North and South America and to centrally planned economies and the major exporter to the Middle East and Africa. The United States is the major exporter to Asia and, along with the United Kingdom, to Oceania. A major part of Italy's export goes to centrally planted economies and France's trade is heavy with its overseas territories.

# CONSUMPTION

i.. The total consumption of plastics has also been increasing in the last decade at the fast rate of 12.5 per cent per annum. Data on apparent consumption are given in table 1.9 for the Western European countries, Japan and the United States indicating that in recent years they consumed about 85 per cent of total world production, although their share has declined in comparison with the early years of the 1950s. The rate of growth in these countries differed. Thus, consumption in Western Europe and Japan has been growing at a faster rate than the United States, and their share in total consumption increased over the last decade from 30 per cent in 1950 to 56 per cent in 1961.

12. With respect to the developing countries available data indicate a low share in total consumption, 3.4 per cent for 1955-1956 and in 1960 a slightly improved share of 5 per cent.

	19 <b>50</b>	/933	1955	1959	1960	1961	1962
Europe (West)							
France	39	65	106	252	340	374	452
Germany (Fed. Rep. of)	98	211	342	641	805	776	1,000
Italy	26	52	84	204	250	334	416
United Kingdom	129	161	226	377	432	474	542
Others	48	82	350	430	572	675	773
SUB-TOTAL	340	571	1,108	1,904	2,399	2,633	3,183
Japan	47	106	141	467	540	694	912
United States	916	1,187	1,614	2,135	2,474	2,650	2,957
Australia			12	34	39	39	- 44
Brasil	4	17	27	52	64	112	100
GRAND TOTAL	1,308	1,881	2,902	4,592	5,516	6,127	7,196

TABLE 1.9. CONSUMPTION OF PLASTICS AND RESIN, SELECTED COUNTRIES, 1950-1962 (Thousand metric tons)

SOURCES: Australia — Commonwealth Bureau of Census and Statistics. "Production Summary No. 3: Plastics and Synthetic Resin, and Plasticizers." Brazil --- Plasticos en Revista. OECD --- The Chemical Industry, 1950. 1962.

TABLE 1.10. CONSUMPTION PATTERN OF PLA	STICS FOR SELECTED	COUNTRIES,	1960
(Percenta	ge)		

Products	Prance	Japan	liety	U. <b>K</b> .	U.S.A.	Australia	Total
Phenolics	8.0	6.1	10.1	10.1	12.2	7.2	10.0
Aminos	8.6	19.7	12.8	12.8	7.0	3.8	10.0
Alkyds		2.7		9,9	9.6		7.0
Polyester		1.7					
Вроку		0.3					
Vinyis	25.7	32.9	20.2	10.8	21.6	40.3	22.0
kyrenes	13.8	4.1	8.1	10.4	17.4	18.7	13.0
obygropylene							
olyuthylene	15.0	8.9	17.1	25.7	18.8	25.6	18.0
Crytics		0.7			2.1	0.5	10
Coumarone-indens.					4.5		3.0
Dellatonics	8.6	1.1	7.0	11.2	1.8	2.1	4.0
Others	20.7	21.8	24.7	9.1	5.0	1.8	12.0
GRAND TOTAL	100.0	100.0	1 <b>00.0</b>	100.0	100.0	100.0	100.0
in thousand tons	330	710	260	480	2.430	39	4.313

Suturcu: See table 1.5.

Loss than I per cont.

# TARKE LILL BREDARED CORRUNCTION FAITHEN OF PLARTICE IN LATIN AMERICAN COUNTNER, 1959

(In metric tons and percentages)

	•	1	•	ł		Celevi	1	a l		Medice	8	Ę		Venezada	1	<b>Tel</b>	3
		Į	1	Ĩ	Per can	ļ	1	1	Per carri	Tons	le e	Tau	Per cen	Jak I	No M	Ĩ	2
	•	ļ	21.0		26.0	1,400	18.0	<u>8</u>	20.0	4,540	18.0	850	25.0	2.700	24.0	23,540	200
	•		2	R	1.0	ŝ	8.0	250	5.0	1,380	5.0	2	2.0			0.11	~
	•	ļ	0.0	3,000	8.0		4.0	<del>9</del>	7.0	1,500	6.0	8	1.0	8	•	7,160	2.0
	•	1,860	10.0	5,000	14.0	8	0.11	997	6.0	2,240	9.0	ş	1.0	4		10.240	10.01
		ŧ	2	8	20	<u>8</u>	20	<u>9</u>	2.0	8		0		904	4.0	1.680	0.0
	• • •	Ş	220		0.61	<del>8</del>	8.0	£	20.0	5,100	21.0	430	13.0	650	0.9	1427-61	
	:		160	4,000	011	1,540	20.0	830	18.0	4,500	18.0	420	12.0	00	8.0	15.190	14.0
		2	1.0	ŧ	2			ŧ	1.0	<b>8</b> 3	3.0			2	•	340	
	•	R	0.1	510	2	<u>8</u>	1.0			2	1.0	8	1.0				
		2	3	200	3	1,530	20.0	750	16.0	2,900	12.0	0.01	31.0	1.150	10.0	001 11	001
		R	92		3.0	8	4.0	8	20	710	3.0	220	6.0	270	2.0	140	0.5
		g	4.0	1,990	6.0	22	4.0	9	4:0	1,000	4.6	220	8.0	4,930	46.0	9,130	0.6
•	PIN		0,401	942'55	160.0	7,680	100.0	4,640	100.0	24,780	100.0	3,430	100.0	11,100	100.0	106,150	100.0

· Less than | per cent. **Bornes: United Resion, BCIA, La Industa Quiniza en America Latina,** vol. 1, p. 942.

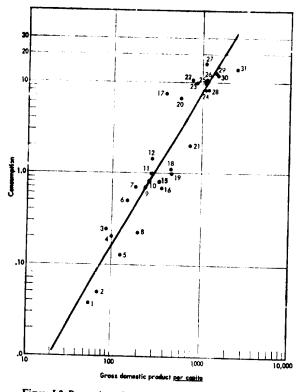


Figure I.2. Per capita, plastics consumption vs. income, 1960

13. Data on consumption by type of products are given in table 1.10 for a number of advanced countries, and in table 1.11 for Latin American countries. These data, by and large, indicate a rather similar consumption pattern, although styrene's share in the Latin American countries is comparatively high.

14. With respect to per capita consumption, data for a number of countries have been correlated to per capita gross domestic product (see figure 1.2). A coefficient of determination of 0.89 was obtained. Regression line was fitted to the data and a linear function to their logarithms gave the following relationship :

 $y = 0.000078 x^{1.65566}$ 

The income elasticity coefficient indicates that on an average, one per cent increase in per capita GDP is associated with 1.7 per cent increase in per capita consumption of plastics. Data for Japan and Italy indicate a much higher per capita consumption than those for countries with a comparable per capita GDP, probably indicating, inter alia, extensive substitution of plastics for alternative materials in the two countries.<sup>1</sup>

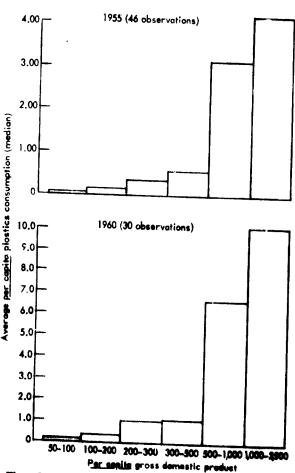
15. A general indication of the effect of factors other than income on *per capita* consumption may be observed in figure 1.3 comparing consumption over time for the same levels of income. The data show that *per capita* consumption has increased by an average of 200 to 300 per cent.

16. As for world potential demand for plastics, excluding centrally planned economies, it may be estimated at 20 million tons in 1975 or an annual rate of growth of 5 per cent.

	Estimated potenti	al demand, 1975
	A	3
Africa .	60,000	100,000
Asia •	370,000	450,000
Latin America	550,000	900,000
Middle East	60,000	100,000
SU <b>B-T</b> OTAL	1,040,000	1,550,000
Western Europe.	8,000,000	
North America	7,000,000	
Others <sup>b</sup>	3,000,000	
TOTAL	19,040,000	

• India's consumption assumed at 250,000 and 300,000 tons respectively.

<sup>b</sup> Oceania, Japan and South Africa.



Pigure I.3. Per capita communition of plantics by income closes.

<sup>&</sup>lt;sup>1</sup> The data show a "jump" in *per capita* consumption, along the regression line, for countries with *per capita* Gi.P crosseding \$300. The countries at the upper quarter of the curve include the six major produces of plastics and the remaining countries in that group produce over 50 per cent of local consumption. Other countries in the produce about 50 per cent and above of their local consumption, except for one, full on or above the regression line. Further investigation, however, is required to assertain more definitely the relationship between *per capita* consumption on the one hand, and local availability of plastics on the other.

17. Estimate A is primarily based on changes in consumption associated with an assumed rate of growth in GDP and population by utilizing the income elasticity coefficient derived above for the sample of thirty countries. A slower rate of growth in *per capita* consumption was adopted for a number of countries at the upper level of consumption that showed, in recent years, a slow-down in the rate of plastics consumption.<sup>4</sup> The population rates of growth are based on those of individual countries in the recent past. In the advanced countries the GDP growth rates used ranged between 3 to 6 per cent. As for the developing countries GDP growth rates ranging from 3 per cent and gradually reaching 5 per cent by 1970 were applied.<sup>3</sup>

18. With respect to estimate B for developing countries, growth rates of 10 to 15 per cent in *per capita* consumption of plastics were assumed for selected countries. These rates comprised the lower boundary for the growth rates recorded in the period 1955-1960 for the thirty sample countries. Much higher growth rates in *per capita* consumption have been obtained for these countries, particularly at levels under 1 kg. The growth in consumption for these countries when related to the respective levels of per capita consumption in 1955

$$\left(\frac{\overline{C}_{40}}{\overline{C}_{45}} \rightarrow \overline{C}_{45}\right)$$

indicated roughly a high growth at low consumption levels that decreased gradually with the increase in consumption.

# END-USES IN PLASTICS

19. In this section, various end-uses as well as recent trends in the application of plastics are being explored. The fields to be covered are construction, packaging, transportation, appliances and plastic pipes and they share about 40 to 50 per cent of total plastics by volume. The data draw on the experience of the United States of America, unless otherwise specified.

# CONSTRUCTION

20. A major share of plastic output goes into this field. For example, the United States consumption in 1961 was estimated at about 737,500 tons, comprising about 24 per cent of the total output. Many types of plastics are used, as indicated in table I.12, most important among which are vinyls, alkyds, phenolics, polyethylene, styrenes and coumaron-indene and petroleum polymers.

<sup>2</sup> The behaviour of per capits consumption was related to per capits GDP over time; for the individual countries in the sample, point elasticity

$$\left(\frac{\Delta \log C}{\Delta \log \Psi} \to \Psi\right)$$

were computed for the years 1955 and 1960 and their deviations from the normal pattern obtained were observed.

\* For more details on the underlying commption see A Sendy of Industrial Growth, 1963 (United Nations publication, Soles No.: 63.E.B.2).

TABLE I.12. TYPES OF PLASTICS CONSUMED BY THE CONSTRUCTION INDUSTRY, 1961

· ·· ·							fat	eric	al.											Percentas of total
Vinyls.																	,			22.5
Alkyds																				16.7
Phenolics	·				•															14.2
Polyethylene	۶.																			12.4
Coumarone-	in	de	ne	а	nd	P	¢tı	rol	¢L	m	pe	oly	m	er						10.8
Styrene .	•																			10.0
Aminos .															÷	÷		Ċ	•	7.1
Polyesiers .													÷		÷	÷	·		•	1.5
Resin											÷			÷		•	·	Ċ	·	1.5
Acrylics											÷			÷			•	·		1.5
Cellulosics.																				0.6
Epoxies								ż	·	·	•		•	·	•	•	·	·	·	0.6
Others •	•	•			•	•			•		÷		•	:	•	•	:		·	1.2
																				100.0
													Te	)T/	NL.	IN		0	NS	737,500

SOURCE: Modern Plastics, New York, Breakin Publications, March 1962, p. 90.

<sup>4</sup> Polyamides, polypropylene, polycarbonates, silicones, polyurethanes.

The end-uses of plastics are also numerous and are given in table I.13, which indicate that the flooring and wall tiles, paints, wire coating and wire devices are the major applications.

21. While the share of plastics that goes into the construction industry is high when compared with total plastic output, the same cannot be said with respect to its importance in the construction industry. In the United States, in 1960, the value of plastic material that went into the construction industry was estimated at \$450 million compared with \$55.6 billion spent the same year for new construction.

22. In this field, attempts have been made to find new applications for plastics and plastics are replacing traditional material such as metals, porcelain, glass,

TABLE I.13. PLANTICE APPLICATIONS IN CONSTRUCTION, 1961

		A	<b>, ppi</b> ti	cath								,				Percentee of total
looring.																23.0
urrace coetings .	•															24.6
																8.8
lectrical equipane	int (	(1034	uol	v i		ملد	tic	m)								14.7
folded Special til	<b>as</b> (	-	ll t	وولأ	. 1	lxt	un	N)								4.6
																5.1
uncis and iamina		•			•	•	•	-						•	•	J.1
loisture barrier, t	ther		l a	nd	20	oie	tu		be	mi	er		-	Ne		8.7
loisture barrier, t lping.	iber	<b>TIN</b>	1 a 	nd	80	ole	tu:	<b>NO</b> 1	ba	mi	<b>er</b>	, 1	•	Ne		
loisture barrier, t	iber	<b>TIN</b>	1 a 	nd	80	ole	tu:	<b>NO</b> 1	ba	mi	<b>er</b>	, 1	•	Ne		8.7

Sounce : Medium Plastice, New York, Breskin Publications, January 1963.

concrete and bricks. The so-called tough plastics, such as acetal, nylon, acrylics, polycarbon, have been competing with metal and porcelain for applications in sanitary ware, sinks, bathtubs and door knobs among others. Plastic pipes and fittings have entered the market, especially drainage pipes, vent pipes, as well as pipes for cold water. Acrylics have also been used in glazing as a substitute for glass in schools and other institutional and industrial buildings where natural lighting is important and breakage constitutes a problem.

23. The trend in a number of countries towards prefabricated units of construction that would be assembled at the construction sites stimulated, inter alia, attempts by the plastics industry in the field. Prefabricated plastic wall panels and structural sandwiches using plastics as part of its material have been experimented with in building construction. To illustrate, plastic wall panels consisting of two translucent polyester glass skins sandwiched over an aluminium grid had been used extensively in the construction of a school in the United States. Although the cost of manufacturing these wall panels is higher than that of manufacturing their equivalent in brick and mortar, the cost is, according to the architects, still competitive when the comparatively iower costs of plastics in assembly and maintenance are taken into consideration.4 The Mexican Government's plan for the construction of 20,000 prefabricated rural schools in the coming decade envisages an important role for reinforced plastics. These schools consist of one large classroom to accommodate 50 students, in addition to living quarters for the teaching staff and family. In these schools, all windows were made of translucent reinforced plastics with decorative motifs; the sanitary fixtures, as well as the spherical water tank on the roof of each school, were also made of molded reinforced plastics.<sup>6</sup> Experiments have also been under way to introduce plastic "shellhouses" as a possibility for low-cost housing. The house wall-panels are made of laminated sandwiches of rigid polyurethane foam, aluminium and hardboard, and the roofs are also made of laminated polyurethane foam between two layers of glass fibres. The "house shell" is fastened by using epoxy adhesives.

#### PACKAGING

24. Packaging is a major outlet for plastics in the United States, consuming in 1963 between 540,000 to 590,000 tons, or about 14 per cent of total plastics output. Plastic is used in a wide range of applications and fields that include packaging food products, textiles, electronic equipment, toys, pharmaceuticals and drugs, detergents and bleaches to mention a few. Important types of plastics used in packaging are given in table 1.14 indicating that polyethylene is the predominant plastic followed next by PVC and polystyrene.

25. A recent trend in packaging is the entry of plastics into the rigid consumers' packaging which is dominated

\* "Plastics Shell House", Ibid., October 1961.

# TABLE 1.14. TYPES OF PLASTICS IN PACKAGING, 1963

				r)	ne												Percentage of total
Polyethylene																	
Polyvinyl Chlorida	•	•	•		•	•	•	1	•	•	•	·	•	•	•	•	51.4
Polyvinyl Chloride	·	·	·	•	·	•	·	·	•	•							23.7
· organgiene	•																12.5
Centrosics																	5.4
Acrylics									•	·	·	·	•	•	·	·	
Polypropylen		•	•	•	•	·	•	·	·	·	·	•	٠	٠	•	·	2.2
Polypropylenc	•	•	·	·	٠	٠	·	·	·	·	·	·	•	•			1.8
nuclai and Copolyn	۱CI	rs -															0.1
Phenolics, Ureas, M	el	an	niı	ne:	8.	•		•	•	•	•		•				2.9
														Γσ	тл	L	100.0

SOURCE: Plastics World, Cos Cob, Connecticul, Cleworth Publishing Co., Inc., April 1964.

presently by glass, metal and paper products. This is evident in the United States by new innovations such as polystyrene packages for cigarettes, polyethylene cases for returnable beverage bottles and test-marketing of polyethylene cans for motor oil, and polyethylene milk bottles. In Europe, a number of innovations have been introduced that include polyethylene oil containers, and bottles for salad oils and vinegar. Milk bottles made from polyethelene as well as from polypropylene and rigid PVC were introduced recently in France and polyethylene wine bottles in Italy.

### TRANSPORTATION

26. Plastics are used in every type of transportation; passenger cars, trucks, buses, railways, boats and aircraft. As table 1.15 indicates, the estimated plastic consumption in the United States in passenger cars alone amounted to about 82,000 tons or an average of 11.3 kg per

TABLE 1.15. PLASTICS USED IN AUTOMOBILES, 1961-1962

											Percentage of total		
			-							_	1961	1962	
Nylon											2.8		
Acrylics								•	•	·		2.5	
Polyethylene .			•	•	•	·	•	•	•	•	5.6	5.4	
Low density	·	·	•	•	·	·	•	•	·	•	9.6	16.5	
Low density.	•	·	•	٠	•	·		•	·	•	(1.6)	(5.0)	
High density.	٠	·	٠	·	٠	•	•				(8.0)	(11.5	
											14.0	12.7	
• myn											24.0		
olyviny! butyra	1.						•	•	·	•		21.8	
cotate and buty	/maj	Ĺ	·	·	·	•	•	·	·	•	2.0	1.8	
ontal		••	•	•	•	•	•	٠	•	·	6.4	5.8	
Cotal.	•	•	•	•	·	•			•	•	0.6	1.1	
	·	•	•	·	·	·	•	•	•	•		5.5	
Others	•	•	·	·	•	•	•	·	•	•	35.0	26.9	
								To	TA	L	190.0	100.0	
n toms	• •										81,580	82.766	

Plaster, 2nd ed. (N.Y., Reinhold Publishing Com. 100

<sup>&</sup>lt;sup>4</sup> "RP Panels for Building Economics", Modern Planics, New York, Breakin Publications, February 1962.

Plastics World, Cleworth Publishing Co., Inc., Cos Cob, Conn., June 1961.

car. Although the passenger car industry is by volume the major consumer of plastics, other transportation facilities are also big users. On the basis of data available, reinforced plastics used in this area were estimated at 11,300 tons in 1961. The total an junt of plastics used in the transportation field constitutes, however, a small share of total plastics output — about 2.5 per cent. Data for the United Kingdom give a similar order of magnitude for the share of plastics used in transportation. In 1962, plastics used in motor cars in the United Kingdom averaged 10.4 kg per car, giving a total consumption of about 12,750 tons.<sup>7</sup>

27. The major uses of plastics in this area are for parts, upholstery and trim. For example, in the United States it was reported that the 1961 cars had about 300 parts made of plastics.

28. In public transportation, plastics found additional applications. For example, in buses and railways they include interior panelling and lining of inner walls and roofs with plastic shrets and laminates; reinforced plastic moulded seats and moulded toilet basins and wash basins. A number of new applications have also been introduced in railways; for example, moulded reinforced plastic doors were used on a small scale in the British Railway system. In France, a panoramic coach constructed for use on tourist routes has a roof and a number of interior mouldings made of reinforced plastics.<sup>6</sup> In trucks, applications include reinforced plastic fenders, headlight section and engine cover. The major applications in aircraft are in acrylics for canopies and windows and reinforced plastics for radomes. Reinforced plastics have been competing on a small scale with metal, especially steel and aluminium, for a share of the body market principally in passenger car bodies and truck cabs. For a small-scale operation it has been found economical to produce bodies made of reinforced plastics in passenger cars, this being attributed mainly to much lower tooling cost, ranging between one-tenth and to one-fifth of the cost of tooling for steel. Furthermore, bodies made of plastics offer greater freedom in the design of body contour, and in addition require a shorter period from design to production;" these factors, combined with the low cost of tooling, allow greater flexibility in the rate of change in models.10 Other advantages offered by automobile bodies are low maintenance and operating costs.

29. Reinforced plastic bodies have been used primarily in the production of sports and other specialized cars of which the output is small. For example, in the United States the earliest user of reinforced plastic bodies has averaged an annual output of 13,000 cars per year own the last five years. Similarly, in Europe, plastic bodies have been used in cars produced on a small scale. 30. In large-scale operations, bodies made of reinforced plastic are non-economical because of the much higher price of reinforced plastics, about four times as much per square foot, because of the fact that the gap in the cost advantages in tooling decreases with expansion in the scale of operation. Estimates of the break-even point for reinforced plastic bodies as compared with steel varies. ranging from 5,000 to 10,000 units per annum. Much higher break-even points have been suggested recently; namely, 72,000 annual production which is based primarily on advantages derived from the additional reduction in total car weight that may be gained over and above the reduction obtained from using plastics.<sup>11</sup>

#### APPLIANCES

31. Broadly speaking, the field of appliances may be classified into major appliances, such as refrigerators, dish-washers, clothes washers, dryers and air-conditioners, and small appliances, such as hair dryers, vaporizers and vacuum cleaners.

32. The plastics used in these appliances include polystyrenes, polyvinyl, phenolics, polyethylene, ABS and polypropylene. Major appliances in 1960 used an estimated 50,000 to 60,000 tons.

33. Plastics enter into the production of a number of parts in refrigerators, meat pans, drains and ice-cube pans, thermostats and parts, inner door panels, egg bins, shelves, to mentior a few. It was estimated in 1962 that about 6.8 kg of plastics have been used per refrigerator. A new trend in this field is the use of urethane foam insulation as a replacement for fibre glass, which results in a substantial reduction of wall thickness. Another recent trend is the replacement of metal in food cabinet liners by high-impact polystyrene, vinyl an J ABS.

34. In washers and dryers, plastics are to be found in a number of applications. Agitators used in washing machines have been made of phenolic for many years. Applications for ABS include agitator caps, detergent caps and housings, vent housings, lint filters, control knobs, etc. Polypropylene is being used in detergent dispensers, filter screens, tanks, tubings, pump housings, etc. Other plastics used in this field include polyethylene and reinforced plastics.

35. In air-conditioners high-impact polystyrene is a predominant plastic. ABS and polypropylene are also used in such applications as escutcheons, grilles and drip page.<sup>15</sup>

<sup>&</sup>lt;sup>†</sup> "Plastics in Great Britain", *Modern Plastics*, April 1963 (New York, Breakin Publications).

<sup>&</sup>lt;sup>6</sup> "Plastice in Railway Rolling Stock", British Plastics, Industrial Publications I.td., London, April 1959.

<sup>\*</sup> This derives mainly from the fact that more time is required to perfect at set of tools for a new model of steel body than for one made of plastic.

<sup>16 &</sup>quot;Plastic Car Bedies", British Plastics, Industrial Publications Ltd., London, Pobrusry 1968.

<sup>&</sup>lt;sup>11</sup> Ibid. In a recent article on the subject, a comparative cost estimate was made for a steel or reinforced plastic body for a typical four-door medium price sedan. It was estimated that the reduction of 400 lbs. might be realized as a result of using plastic bodies, and as a corollary to that, an equivalent weight eaving might be obtained thus reducing the total weight of the car by 900 lbs. On this beats and assuming a three-year tooling cycle, the break-even point was estimated at 72,000 units per year. (H. H. Chapman, "The Boonomics of Fiber Class Reinforced Plastic in Autr-motive Bodies", Paper delivered at the 10th Annual Technical and Management Confirence of the Bosisty of Plastics Industry, February 5-7, 1963.)

<sup>18 &</sup>quot;The Coming Market in Appliances", Medern Plastice, New York, Breakin Publications, July 1962.

36. Small appliances use plastics extensively. There are a number of these appliances of which a great part is made almost exclusively from plastics; for example, some hair dryers and vacuum cleaners are made almost completely of plastics, except for the motor.<sup>13</sup>

# PLASTIC PIPES

37. Plastic pipes and fittings have grown at a remarkably high rate in the last decade. Their share in plastic output, however, is still small, about 1 per cent in 1961. As table I.16 indicates, polyethylene pipes predominate amounting to 60 per cent of the total. Other pipes include those made with ABS, PVC, cellulose-acetate-butyrate, acetals, nylons, fluorocarbons, polypropylenes, and pentaerythritols.

TABLE I.16. PRODUCTION OF THERMOPLASTIC PIPES AND FITTINGS

	Percense	Percentage of total	
	1960	1961	
Polvethylene	59.0	59.5	
PVC. ABS	10.2	15.5	
Ruivrate	11.8	11.9	
Bulyrate All others.	1.7	1.2	
· · · · · · · · · · · · · · · · · · ·	11.8	11.9	
Total	100.5	100.0	
n lons	30,800	38,100	

August 1962. Modern Plastics, New York, Breskin Publications,

38. Pipes are used in numerous applications that include water distribution, sewer and drain pipes, industrial and chemical pipes, gas distribution, oil-field piping, and electric conduit. The use of pipes for water distribution, mainly cold water, is the largest volume outlet for plastics. The recent trends towards producing plastic pipes in wide diameters made possible their use in a number of countries in water mains although still on limited scales. The next biggest use for plastic pipes is in the industrial and chemical fields, and an important advantage of plastic pipes in this field derives from their excellent corrosion resistance to salts, acids and alkyds. An early use of plastic pipes was in gas distribution, and their greatest advantage over metal pipes is lower maintenance cost. In oil fields, plastic pipes are being used primarily in gathering lines for sour crudes, salt water disposal system, and lines that have to be run through aggressive soils.14

39. By and large, pipes made of plastics have the advantage over a number of their competitors of lower installation and operating costs. Further, their inertness

to a wide range of chemicals constitutes an important factor in certain applications. Other advantages include light weight, electrical non-conductivity, low thermal conductivity, and flexibility. On the other hand, the relatively low bursting pressure, the limited maximum diameters and greater degradation of some pipes when exposed to light as compared to metal pipes are among the important factors limiting their usefulness in many applications. Furthermore, while their electric nonconductivity and low conductivity of heat are important characteristics in certain areas, they may be considered limiting factors.<sup>16</sup>

## OTHER USES

40. Plastics are used in numerous fields and applications, and it is not intended in this short presentation to be comprehensive. Mention of a number of these fields may be in order.

41. The use of plastics in the field of furnishing is well established and new applications are found. Laminates, such as formica, are used in making furniture in homes, and offices, as well as in institutional and industrial establishments. Molded plastics of such material as reinforced plastics, polyethylene and ABS are used in seatings for schools, institutions and similar fields where high performance in respect to durability, resistance to shock and vandalism, as well as ease of maintenance are needed.

42. The inertness of plastic material to certain chemicals have been put to use in the production of tanks and containers for use in shipping, storage, and chemical processing of various types of liquids. Reinforced plastic railroad tanks have been introduced on a limited scale for transporting chemicals. Large capacity tanks have been attained; 5CO-gallon polyethylene tanks have been reported recently. Polyethylene tanks are being used in the fields of chemical processing and metal plating.

43. In the field of non-durable consumer goods, plastics show in many applications. They are used in various types of footwear in the form of soles as well as other components. Shoes completely molded of plastics are also being made, but PVC is the predominant plastic in this field. Other plastics such as ABS, polyethylene, polystyrene, polypropylene and acrylics are also used.

44. Dinnerware molded of melamine and manufacturing of toys and sport goods are already established fields of application. Other applications are so diverse that they include the medical field, where plastics have been used as replacement in part or whole of various organs and structures of the body. The electrical, electronics and missiles fields, also make wide use of plastics.

# PROPECTS IN DEVELOPING COUNTRIES

45. In developing countries the applications of plastics are by and large similar to those in advanced countries, although there is greater concentration on non-durable

<sup>&</sup>lt;sup>18</sup> "Trends in Housewares", Modern Plastics, New York, Breskin Publications, September 1962.

<sup>&</sup>lt;sup>14</sup> "Plastic Pipes, a New Plateau", *Modern Plastics*, New York, Breekin Publications, August, September 1962.

<sup>&</sup>lt;sup>15</sup> "What you should know about plastic pipes", *Mill and Factory*, Conover-Mast Publications, Inc., New York, October 1961.

consumer goods. The potentialities of plastics in certain fields in developing countries naturally differs from one country to another, depending on economic, technical and other factors including, *inter alia*, the scarcity or abundance of plastic substitutes, government policies, and acceptance of plastics by the various users.

46. Further investigation, however, is needed to ascertain the growth potentials of plastics in specific fields, taking into consideration the complex interaction of these factors. Such fields may include building construction, transportation, plastic pipes for irrigation and water mains, and packaging.

#### II. Synthetic fibres

#### PRODUCTION AND TRADE

47. World production of synthetic fibres has increased from 73,000 tons in 1950 to 1,080,000 tons in 1962, at an average growth rate of 21 per cent per annum. The major producing countries are the United States of America, Japan, the United Kingdom, the Federal Republic of Germany, France and Italy, sharing in 1962 about 86 per cent of total output. The United States is the major producer, although its share has been declining. A faster rate of growth than that of the United States (15 per cent per annum) has been recorded in recent years by a number of producers of synthetic fibres and they have been increasing their share, thus Western Europe and Japan (30 per cent per annum growth rate) raised their share of total world output from 16.8 per cent in 1950 to 50 per cent in 1962 (see table II.1). A number of developing countries, including Mexico, Argentina, Brazil, the United Arab Republic and India, began production and in 1962 shared about 1.5 per cent of world output.

48. An analysis of world production of synthetic fibres by types indicates that nylon is still the predominant fibre, followed by acrylic and polyester (see tables 11.2 and II.3). Nylon has recorded a decline in its share, from 60 per cent in 1959 to 55 per cent in 1963, while polyester showed, for the same period, an equal gain, 14 per cent to 20 per cent respectively. For the major producing countries, in addition to nylon as the major product, each country tends to favour a second fibre that has been developed locally, such as Merinova in Italy, Vinylon in Japan, and Terylene (Dacron) in the United K<sup>2</sup>agdom.

49. With respect to trade, the major producers mentioned above, in addition to Switzerland, are also the major exporters, sharing about 90 per cent of total export. The United States is the major exporter of synthetic fibres; its share has however been declining, while the share of the remaining major exporters has increased greatly (see table II.4).

50. With respect to import, Western Europe remains the major importing region. Its share in total imports increased from 40 per cent in 1951 to 67 per cent in 1960. Other regions experiencing an increase in their share are Asia, Africa and centrally planned economies. North America's share, however, has been declining, along with that of Oceania and Latin America, reflecting primarily, in the latter two regions, the rapid development of local production facilities in Australia and three big Latin American countries (see table II.5).

TABLE II.1.	WORLD	PRODUCTION	0¥	SYNTHETIC	FIDRES,	1950-1960
		(In thous	عاتها	( tone)		

	1990	1951	1952	1954	1956	1958	1939	1940	1961	1962
North America										
United States of America	55.52	77.38	<b>95.5</b> 7	129.13	181.62	222.49	<b>292</b> .71	307.17	140.41	
Others	2.27	2.81	3.67	5.53	7.03	9.80	13.47	16.46	340.61 19.32	440.17 22.5
SUD-TOTAL	57.79	80.19	99.24	134.66	188.65	232.29	306.18	323.63	359.93	462.75
Western Europe										
France	1.68	2.90	3.32	7.62	14.83	23.36	32.75	45.27	an na	
Germany (Fed. Rep. of)	0.91	2.99	3.99	7.44	14.05	24.49	38.64	43.27 52.57	51.35	65.45
Italy	0.54	2.09	2.13	7.85	11.64	18.78	25.08		65.27	94.03
United Kingdom	4.45	5.90	8.03	12.02	23.00	30.30		33.70	43.46	63.28
Others	0.95	1.63	2.04	4.44	7.79	11.80	39.87 16.69	61.69 21.85	67.36 27.53	84.05 41.60
SUB-TOTAL	8.53	15.51	19.51	39.37	71.31	106.81	153.03	215.08	254.97	346.41
Japan.	3.72	3.17	3.54	9.70	28.80	46.36	66.79	118.30	1 <b>53.09</b>	182.35
Other countries	3.09	5.77	7.49	13.44	21.60	29.66	35.63	47.72	69.76	85.99
GRAND TOTAL	73.13	104.64	129.76	197.17	300.36	417.12	575.63	704.73	837.75	1.079.50

Sconers: 1950-1960; FAO, Per Caput Fibre Commenters, Rome. FAO, Commently Bulletie, Series 31, Rome 1968, and FAO Monthly Bulletie of Agriculture? Beaumics and Statistics, 7- wary 1962 and April 1964. Textile Organon; Tentle Sociomics Bureau, Inc., New York.

		1939		1960		1961		1962		
	Tens	Per cen	Tons	Per cent	Tone	Per 100				1963
Acrylic =							Tone	Per cent	Tone	Per cel
Western Europe Americae	14.5	14.6	30.4	23.7	38.1	27.0				
All others	<b>65</b> .3	65.4	64.9	50.5	65.3	27.0	59.0	32.2	66.2	30.8
	20.0	20.0	33.1	25.8		46.3	78.9	43.0	98.4	45.8
-		·			37.6	26.6	45.4	25.8	50.3	23.4
Nylene Total.	99.8	100.0	128.4	100.0	141.1	100.0	183.3	100.0	215.0	100.0
Western Europe	96.6	28.4	127.0						41.º.V	100.0
Americas	191.4	56.2		31.7	149.7	31.5	197.8	32.9	246.2	
All others	52.2	15.4	205.0	51.2	240.9	50.7	306.2	51.0	246.3	33.6
		13.4	68.5	17.1	84.4	17.7	96.6	16.1	349.3	47.6
TOTAL	340.2	100.0						10.1	137.9	18.8
rolyester	540.2	100.0	400.5	100.0	474.9	100.0	600.6	100.0	733.5	
Western Europe	28.1	34.0					-		133.3	100.0
Americas	40.4	49.0	41.7	36.6	48.]	34.5	66.7	34.2		
All others	14.1		49.4	43.4	50.3	36.1	75.7	38.8	90.3	34.6
	14.1	17.0	<b>22</b> .7	19.9	40.8	29.3	52.6	36.8 27.0	100.7	38.6
TOTAL	82.6	100.0	113.9					47.0	69.9	26.8
Other Fibres		100.0	113.9	100.0	139.3	100.0	195.0	100.0	260.8	100.0
Western Europe	13.6	25.0	14.0						490.9	100.0
	13.6	25.0	16.8	25.0	19.1	23.1	24.9	24.7	<b>30</b> a	• • •
All others	27.2	50.0	13.2	19.7	14.5	17.6	18.6	18.5	29.9	24.4
_			37.2	55.4	<b>50</b> .0	60.5	57.2	56.8	24.5	29.0
TOTAL	54.4	100.0	67.1						68.0	<b>55.6</b>
hand total		100.0	0/.]	100.0	82.6	100.0	100.7	100.0	122.5	100.0
Western Europe	152.9								144.3	100.0
Americas	310.7	26.6	215.9	30.4	254.9	30.4	348.4			
All others	113.4	<b>53.8</b>	332.5	46.8	371.0	44.3		32.3	432.7	32.5
	413.4	19.6	161.5	22.7	211.8	<b>25</b> .3	479.4	44.4	572.9	43.0
TOTAL	577.0	100.0	300.0			<b>~~</b>	251.7	23.3	3 <b>26</b> .1	24.5
		100.0	709.9	100.0	837.8	100.0	1,079.5	100.0	-	

## TABLE II.2. WORLD PRODUCTION OF SYNTHETIC FIRES, BY TYPES AND REGIONS (In thousand tons and percentage)

Unca: Texelle Organon, June 1963, June 1964.

·) includes in modecrylic.

51. Trade has been increasing at a faster rate than production; roughly 30 per cent per annum over the last decade. Consequently, its share in total output has also been increasing from about 6 per cent to 17 per cent. Data on the major types of synthetic fibres that enter trade are not readily available. The share, however, of total export in local production in the major exporting countries is given in table II.6 indicating for a number of countries a high share in production. With respect to Switzerland, which is not a major producer, synthetic Shees are imported for further processing and re-export.

### CONSUMPTION

52. World consumption of synthetic fibres has also been peasing at a fairly high rote, about 20 per cont per annum. The growth of consumption in the various regions didler. North America, principally the United States of America, recorded a slow rate of growth and its share in total consumption has green declining, whereas the remaining regions of the world recorded a higher share in world consumption (see table II.7).

\*) Azion, nytrii, olofin, aran, spanden, vinyi, vinyon.

53. The advanced countries of North America, Western Europe and Japan are the major consumers, sharing over 85 per cent of world consumption; the developing countries shared only about 4.5 per cent in

54. The important single factor explaining the differences in consumption is per capits income. The average relationship between per capita consumption and per capits income has been tested for a sample of thirtysix countries and the data yielded a coefficient of determination (R<sup>4</sup>) of 0.72. A logarithmic equation was fitted to the data showing a functional relationship as follows:

y = 0.0000403 x 1.00077 (see figure II.1)

55. Income elasticity coefficient (d) indicates that on an average, 1 per cont increase in per capita income is associated with 1.37 per cent increase in per of consumption. Several tests have been applied to these nita data to establish the relationship between differences in climates or local supply conditions (ratio of local pro-duction to consumption) in the various countries and duction to consumption) in the various countries and per capile consumption. These data, however, did not

	1951	1954	1956	1958	1959
lialy	(2.2)	(7.8)	(11.4)	(18.6)	(25.4)
Nylon	0.9	3.2	7.3	12.7	19.5
Merinova	1.3	3.6	3.2	4.1	2.7
Others	-	_	0.9	1.8	3.2
lapan	(3.2)	(9.5)	(28.6)	46.3	80.7
Amilan (including Nylon).	0.5	4.5	15.4		
Vinyl Fibres	2.7	4.J 5.0		23.2	30.8
Acrylic Fibres	4.7	3.0	13.2	17.2	23.1
Others (Polyester, Polyethylene)				2.7	12.2
				3.2	14.6
Inited Kingdom	(5.0)	(11.4)	(23.2)	(30.0)	(32.0)
Nylon	5.0	9.5	15.9	21.3	25.4
Decron		0.5	5.9	8.2	11.3
Acrylic and others		1.4	1.4	0.5	2.3
inited States	(77.7)	(129.3)	(181.5)	(222.7)	(292.5)
Nylon	65.3	92.1	117.9	•	
Dynei.	1.8	2.3	117.9	1 <b>36</b> .1	176.9
Saran	5.9	16.3	10.9	-	
Vicara	0.5	0.9		9.1	4.5
Orion	3.2		_		-
Acrilon	0.5	9.5		<u> </u>	
Decroel .	0.5	1.4	35.4	48.1	63.5
Vinyon .	-	5.4	-	_	<u> </u>
Polyester		0.9			
		_	14.1	24.9	36.3
	0.5	0.5	3.2	4.5	11.3

## TABLE II.3. ESTIMATED PRODUCTION OF NON-CELLULOBIC PIERGE BY TYPES, IN SELECTED COUNTRIES (In thousand tons)

Sounce: United Kingdom, Commonwealth and Economic Commission, Industrial Pibres.

## TABLE ILA. EXPORT OF SYNTHETIC PHRAM, 1951-1962 (In thousand tons)

	/ISJ	1953	1954	1956	19 <b>5</b> 8	1939	1960	1961	1962
United States of America	4.19	3.\$7	6.53	13.82	18.26	27.44	36.97	36.34	43.07
-									
Prase	0.72	0.64	1.89	3.05	4.15	6.66	10.26	14.07	
Germany (Ped. Rep. of)		1.21	1.75	3.49	11.03	16.62	20.01	14.07	18,41
Italy.	0.30	0.25	0.93	1.61	3.86	7.64		44.10	35.5
Switzerland .	0.13	0.25	0.57	1.26	3.29	4.99	12.83	21.27	35.00
United Kingdom	0.85	0.85	1.41	3.30	3.45	5.79	8.39	10.49	14.3
Others.	9.65	6.30	1.24	2.56	4.82		7.32	10.91	24.0
THE FOTAL	1.73					7.58	13.44	22.42	33.2
	1.13	3.49	7.79	15.27	30.60	49.28	72.25	103.26	106.54
<b>Japan</b>	9.65	9.67	0.16	0.96					
			0.07	0.56	2.63	4,31	8.25	13.70	20.41
Sub-Total	-				0.72	0.63	0.99	1.04	
	0.05	6.67	0.23	1.54	3.35	4.96	9.24	14.74	
<b>Other examples</b> the state of a state of a	6.61	0.01	0.23	0.41	0.64	0.84	1.21	1.43	•••
CAND TOTAL	6.18	7.14	14.78	31.84	52.65	8.9	119.67	155.77	265.71

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## TABLE 11.5. IMPORTS OF SYNTHETIC PERIOD BY REGIONE, 1951-1961

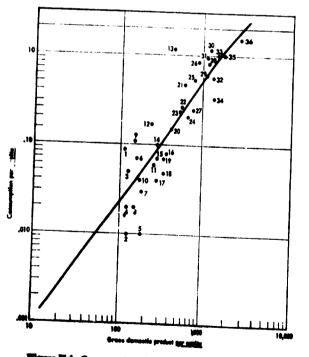
(Percentage)

	1951	1952	1954	1956	19 <b>36</b>	1939	1960	1961
North America Western Europe Oceania Latin America Near East Asia. Africa. Centrally planned economies	9.11 39.61 21.60 22.70 2.30 0.60 3.80 0.20	16.70 39.60 17.00 20.10 1.70 1.50 2.90 0.50	17.50 42.80 11.10 17.40 1.10 4.00 5.40 0.70	17.80 44.60 10.00 12.50 2.00 6.20 6.30 0.60	7.10 45.50 9.00 10.40 3.70 13.00 8.60 2.70	6.83 55.44 4.50 12.70 4.30 8.20 5.70 2.50	4.00 66.50 3.90 6.90 2.30 9.30 4.70 2.40	5.65 59.93 4.06 8.86 3.49 8.63 6.36 3.02
GRAND TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

SOURCE: 1951-60: FAO, Per Caput Fibre Consumption; Rome. FAO, Commodity Bulletin; Series 31, Rome 1960, and FAO, Monthly Bulletin of Agricultural Economics and Statistics, January 1962 and April 1964. Textile Organon; Textile Economics Bureau, Inc., New York.

TABLE II.6. EXPORT A	S PERCENTAGE OF	PRODUCTION FOR	MAJOR	EXPORTING COUNTILIES
----------------------	-----------------	----------------	-------	----------------------

	1952	1954	1956	1958	1959	1960	1961	1962
United States	3.7	5.1	7.6	8.2	9.4	12.0	10.7	9.8
France	19.3	24.8	20.6	17.8	20.3	22.7	24.4	28.2
Germany (Fed. Rep. of)	23.2	23.5	21.8	45.0	43.0	38.2	36.9	37.8
Italy	11.7	11.8	13.8	20.5	30.5	38.1	48.9	55.3
Switzerland	55.6	33.1	51.4	90.6	98.2	125.0	127.0	125.1
United Kingdom	10.6	11.7	14.3	11.4	14.5	11.9	16.2	28.6
Japan	2.0	1.6	3.4	5.7	5.3	7.0	8.9	15.6



SOURCE: Computation based on tables.

Figure II.1. Communities of synthetic filres per capita ve. income, 1960 yield a pattern or a significant average relationship for the above two factors. This, however, does not negate the existence of such relationships because in each country a multiplicity of factors usually effect the consumption and in different directions<sup>16</sup> such as customs, substitute materials and local supply conditions; the trend in several countries towards lighter garments because *inter alia* of widespread heating of houses, offices and factories as well as means of transportation<sup>17</sup> and casual dressing, etc. The effects of factors other than income may be observed in figure II.2 which shows the increase overtime in *per capita* consumption at

<sup>&</sup>lt;sup>17</sup> Synthetic fibres are generally lighter than other types of fibres. This may be illustrated partly by the concept of poundageutility which measures differences between various types of dives taking into account such considerations as strength to built ratio and difference of waste in manufacturing. Pounds of cotten that may be considered roughly equal to one pound of man-made fibre are given as follows:

Layon and sostate: Bagele and tow. Planet pers: Elight tensity Regular and inter-			•	:	:	•	:	1.37
manifeld tenacity			•	•	•	•	٠	1430
	1.34	Giana						4 44

<sup>&</sup>lt;sup>16</sup> For a detailed treatment of various factors and particularly qualitative factors that affect textile fibres consumption, see: Studies of Factors Affecting Communities of Textile Fibres, part II published by the International Cottom Advisory Committee, Washington, July 1960.

TARLE IL7. CONTRACTION OF SYNTHETIC PROM

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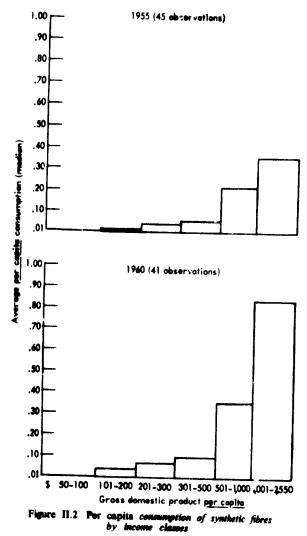
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	•	< 1 1	4 83	41	1	21	1	21	1	15	1	1	1	21	1	21	1	1		1		121
	<b>K</b> 1 <del>-</del>	3 1 2		292	323	2=3	2151 14 14	322	1.1 1 1 1 1 1 1	<b>3</b> 25		202	215 215 215 215		323	1.0.X		4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4		19.1 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1	11.14 14.14 18.14 19.15	1 11
	•••	92	925 92	<u> </u>	233	872		533	21.9 5.7 8.9	322	2221	352	27.8 8.7 2.2	312	33.3 14.6 3.7	323	14 <u>15 1</u> 17 10 1	323	22 A	7.1 3.0 7.0	73.7 21.5 4.6	333
	•••	<b>2</b> 7	2 4 4	23 23	23	21		43	22	23	41.5 2.4		13	<b>1</b> 5	7.0	13.4	19 19 19	15.7 13 1.5 1	<b>19.9</b> 12.2	16.7 1.5 2	33	<b>4</b> 2
				3	3	0.2	23	23	9.0 9.0	2 G 2 G	<b>9</b> 9.	22	56	23	512	33	22	33	5 9 	4 6	19 6 19 9	9 <b>9</b> 2 C
<b>1</b>			1	IN MI IN		ł		2	319.5	ì			419.2 H		574.9 H	K 0.	703.6	68 0.00	836.5 10	1.0.00 1.000 S.S		Ì

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constant income levels. These data indicate that consumption has about doubled for all income classes and for the \$100-\$200 category consumption has quadrupled.

56. The relationship between synthetic fibres and total textile fibres is given for the various regions of the world in table II.8. These data indicate the increasing share of synthetic fibres in total textile fibres reflecting primarily substitution of the former for other types of fibres. This relationship when compared to per capita GDP for the sample of thirty-six countries for the years 1955 and 1960 showed a significant coefficient of correlation : R = 0.72 in 1960.<sup>16</sup> Comparing this relationship for the same years, the curve showed an upward shift that

averaged about 5 per cent. The data indicate also a distinctly high ratio of synthetics in Japan and low ratios in Australia and New Zealand. This reflects, in part, the range of substitution as dictated by availability of substitute fibres on the local markets. Further, it may be noted that while a significant correlation seems to exist between the ratio of synthetics in total textiles and income, in contrast, no similar average relationship can be ascertained for rayon.

57. With respect to future requirements of synthetic fibres, it was estimated that by 1975 the total world potential demand may reach about 2.5 million tons compared with about 1 million tons in 1962 or an increase of about 2.5 times.

53. Estimates of potential demand for synthetics have been based on projection of total fibres consumption by regions and major countries published by the International Cotton Advisory Committee. These projections

Estimate of synthetic fibres requirement by major regions, 1975

					•				- / //		
									i	P62	1973
									( In	thousand	herus)
Asia										A	
India									5	35	70
Rest of Asia.									20	55	100
Africa									7	45	90
Latin America.									32	130	200
Middle East.	•				·		·		5	35	65
				Sı	<b>.</b>	T	<b>TA</b>	L	70	300	525
North America.						٩			440	1,000	
Western Europe									320	800	
Others *							·		170	400	
		G	<b>R</b> /	<b>NN</b>	D	TO	TA	L 1	.000	2.500	

· Oceania, Japan and South Africa.

were given for the year 1970 and estimates for 1975 have been made using primarily the same underlying assumptions.10 Assumed shares of synthetic fibres in total fibres have been assigned for the various countries in each region and two sets of assumptions were made with respect to the developing regions of the world."

59. Direct methods, similar to those applied for plastics, for projecting potential demand were used and

by 1960, <sup>20</sup> The average share of synchotic fibres in some first and the assumed averages for 1975 are as fo n fr year 1962 and the ann

Ania										1962	19	<b>#5</b>
India											A	
and the second second	٠	•	٠	٠	•	•	٠	•		0.5	2.5	5.0
Pekinen Rett of Asie	•	٠	·	•	•	•		•	•	R.A.	2.5	ü
A A A A A A A A A A A A A A A A A A A	•	٠	÷	·	•	٠		•		- 14	6.3	114
Landon American	٠	٠	·	٠	•	•	•			1.1	5.0	10.0
Sales America.	•	٠	٠	•	٠	•	•		•	2.7 (1961)	1.6	ille
	٠	·	٠	٠	•	•	•	•		1.1 (1961)	6.5	11.1
Marth Agerica	•	٠	٠	٠	•	٠	•	•		13.1	20.0	- MA
wanten secon	• •	٠	•	•	•	•	•	•	•	16.1	13.0	

<sup>&</sup>lt;sup>36</sup> The curve that yielded the best fit for the data in 1960 was ated as follows:

<sup>- - 11.12</sup> X 5.08 log X X.

Ø, - share of synthetic - per capite GDP) ics in total textile fibres)

This relationship indi to date for 1955 did not yield similar relations in the share of a pitch may be needed to assertain the database. Puri intensities on the seeded to assertain the database. s an increase in the share of syn ia GDP. hip on the tempo of the feture growth in

<sup>10 &</sup>quot;Prospective Trends in Co ħ International Cotton Advisory Ce 1962, and "Studies of Pactors Affe w. - 0 International Cotton Advisory Cos Fibres' July 1960.

	1930	195 .	1952	1954	19 <b>36</b>	1937	1958	1939	1960	1961	1962
North America	1.7	2.4	3.3	4.8	4.0		• •				
Doenia.		0.8			6.0	8.1	8.0	8.9	9.6	11.0	13.1
Western Europe			1.1	1.7	3.3	3.4	4.6	4.1	4.6	5.9	7.1
Centrally planned sconomies	0.4	0.7	1.0	1.6	2.8	3.5	3.8	5.1	7.0	8.1	10.1
Incl. China (multitud)											10.1
Incl China (mainland)	0.1	0.2	0.3	0.4	0.6	0.7	0.7	0.7	1.0		
Excl. China (mainland)	0.2	0.4	0.5	0.7	1.0	1.1	1.1		1.0	1.4	
atin America		0.2	0.2	0.5	-			1.2	1.6	1.9	
fiddle East		0.4			0.7	0.7	1.1	1.7	1.8	2.7	
BPBA				0.1	0.3	0.4	0.5	0.9	0.7	11	
aot Asia	1.6	0.8	0.7	17	3.7	5.3	7.4	97	11.7	12.1	15.7
	A. 60.00				0.1	0.2	0.4	0.4	0.6	0.7	1.4
outh Africa		0.2	0.5	1.0	2.2	1.9	2.6	2.5	27		
est Africa				0.1	0.3	0.5			- ·	4.1	6.0
				<b>U</b> . I	0.3	0.3	0.9	1.0	1.0	2.1	2.2
GRAND TOTAL	0.7	1.0	1.2	17	2.4	3.1	3.1	3.9	47	5.5	6.9

## TABLE 11.8. SHARE OF SYNTHETIC PIBRES IN TOTAL TEXILE PIBRES CUNBUNPTION BY REGIONS, 1950-1962

(In percentage)

SOURCE: 1950-1960: FAO, Fer Caput Fibre Consumption; FAO, Commodity Bulletin, series 31, Rome 1960 and FAO, Monthly Bulletin of Agricult-ural Economics and Storiestics, January 1962 and April 1964. Textile Organon, Textile Economics Bureau, Inc., New York

were based on the analysis of data for a sample of thirtysix developed and developing countries for the years e 1955 and 1960.11 The results were found to be rather unsatisfactory when compared with the most recent data on actual consumption and production.

<sup>11</sup> These estimates were based on an assumed income electicity coefficient equal to 1.37 and similar assumptions to those made for plastics with respect to growth in GDP and population. Point electicity over time was computed for the sample and the growth in per ceptie consumption was also related to the level of per ceptie income, see paragrephs 17 and 18. With respect to the latter, the data did not yield meaningful average relationship.

production have	estimates exclude c on estimates of co been made available igary and Yugoslavia	noumption and
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						Pred	iscillen	Conn	nytion
						1970	1975	1970	1075
							(In these	and tone)	
Hungary		,				11-12	····	14-15	
Yugoslavia	,			•		7.3	26.6	18.0	28.0

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TABLE II.9. B	SND-UBBS IN	SYNTHETIC	Filesas,	UNITED	STATES	07	AMERICA
---------------	-------------	-----------	----------	--------	--------	----	---------

	ÂN			
	? <b>\$48-1984</b>	1963-1940 Personinge	1961	1962
	(58.8)	(41.1)	(37.8)	(36.0)
Men's and boys' wear	11.9	11.9	13.1	13.2
Worsen's, misses' and juniors' wear	36.0	26.1	21.9	20.2
Cirls', children's and infants' wear	2.1	3.1	2.8	2.6
fome flouishings •	8.2	15.9	21.5	22.9
ther communitype products because a second	2.6	5.2	5.8	5.8
ndustrial area,* total and a second second second	39.2	37.8	34.5	
Types alone		37.0		35.3
			(15.3)	(15.9)
TOTAL	100.0	100.0	100.0	108.0

n. Inc., New York. December 1963.

14 N is, and pi H, IPHI k, camputs and rage, metalos.

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#### END-USES IN SYNTHETIC FIBRES

61. Data on end-uses of synthetic fibres are available for Japan and the United States of America and indicate that a good share of synthetic fibres goes into industrial uses, although apparel and household uses are still the major consumers (tables 11.9 and 11.10.) The United States data show a decline in the share of apparel and to a much lesser extent in industrial uses whereas home furnishing and other uses increased their share. In Japan, on the other hand, synthetic fibres in apparel and household uses, recorded a decrease in their share of the market, although they increased their share in industrial uses. However, consumption in the latter applications are still lower in Japan than in the United States of America

#### TABLE 11.10. CONSUMPTION OF SYNTHETIC FIBRES IN JAPAN BY END-UNES

Percentage distribution

	Apparel and household uses	Industria uses	Tei i
1952-54			
Average	80.5	19.5	100.0
t <b>955-6</b> 0			100 0
Average	78.7	21.3	100.0

SOURCE Prospective Trends in Consumption of Textile Fibres, International Cotion Advisory Commiller (Washington, 1962) • Major industrial uses are rubber goods, fishing nets and electric wires.

62. Comparing the share of synthetic fibres in industrial uses with that of total textile fibres, the former's share is still higher (see table II.11), which is attributed, inter alia, 10 the superior properties of the former type of fibres which include durability, strength and chemical resistance.

TABLE (1.11. ESTIMATE OF TEXTILE PIBRE CONSUMPTION IN THE MAIN END-USES, SELECTED COUNTRIES

	Clothing	consumption	Industriai of total fibre in quantity 1954-1957)
Beigium-Luxembourg	59	25	26
France	57	21	22
Germany ("od. Rep. of).	60	21	19
Italy	58	28	14
Netherlands	54	33	t <b>4</b>
Sweden	60	23	17
United Kingdom	50	25	25
Average of above	56	24	20
United States of America	54	24	22
Papara a construction a construction	9	0	10

BOURCE: Studies of Pactors Affecting Communica of Textile Pibres, International Cotton Advisory Committee (Washington, July 1960). Per Japan: Data Remidted by Tuntile Bureau, Ministry of International Frede and Industry, Japan.

63. Inter-fibre competitions have been affecting the pattern of distribution of the various types of fibres among the different end-uses. As observed above, synthetic fibres have been gaining ground over other types of fibres (see table 11.8) This gain is attributed to a number of factors that include better properties of synthetic fibres in a number of end-uses, as well as to the greater reduction. in general, of the prices of synthetics, over the years, as compared to other types of fibres or a combinalion of these factors. Synthetic fibres are considered, by and large, strong, durable, light, non-absorbent and resistant to chemicals Further, certain properties of synthetics have been used to complement properties in other fibres, i.e., by blending of cotton and nylon the fibre obtained will dry more readily than cotton alone, blending of wool and nylon yields an increase in strength, durability, wet stability and dimensional stability, and wool with polyester gives crease resistance and permanent pleats properties

64. The more detailed data from the United States of America and Japan confirm the trends in the share of synthetics in each of the main end-uses (see tables 11.12 and 11.13). A number of interosting observations may be made with respect to these data. In the United States, cotton recorded a net gain in apparel whereas wool and rayon were losing ground. The gain recorded by cotton is primarily attributed to technological advances in the finishing of cotton fabrics such as the development of shirts requiring little or no ironing. Wool has been losing ground to cotton and other lighter man-made fibres because of the general trend for light garments in the United States and in spite of the fact that prices of wool have declined more rapidly than those of other types of fabrics.<sup>38</sup>

65. In Japan, on the other hand, cotton's share in apparel and household declined while wool and rayon maintained their share of the market. Cotton in apparel has been losing ground primarily to synthetic fibres and wool. The faster decline in the prices of the latter two fibres as compared with cotton and the rise in *per capita* income that transferred demand into higher priced clothing containing more wool blended with synthetic fibres are the main factors contributing to these trends.<sup>36</sup>

66. With respect to industrial uses in the United States, synthetics have been gaining ground over cotton and rayon. The main end-uses in this field are in tyres, where cotton was gradually replaced, at the beginning

<sup>18</sup> Following is the price index for major types of fibres in the United States:

	1	/ <b>m</b>	r			Raw cotton	Raw wooi	Staple Alpen	Stapic Artist	Aorylic Haple	Orien
1951 1953 1955 1957 1959 1961 1963 1964	•				· · · · ·	100.0 79.5 84.3 81.9 80.4 78.4 81.2	100.0 63.8 52.0 59.4 45.0 43.5 48.7	100.0 87.5 85.0 75.0 80.0 67.5 67.5	100.0 100.0 85.0 72.2 72.2	100.0 100.0 75.7 60.5 62.8	100.0 t 00.0 78.9 67.4 67.4
		•	ʻ.	1	•	<b>80</b> .2	<b>53</b> .1	70.0			

Organon, Tuntile Bosmornics Interest Inc., How York.

<sup>10</sup> Comparing 1952 and 1959, the retail price index of woollen fabrics declined from 100 to 75, woollen fabrics declined to 66.1 per cent and the wholesale price of sylan fabrics to 57.0 per cent. TABLE II.12 UNITED STATES TEXTILES PERES. CONSUMPTION BY END-USES

				Man-made	Piller	_
		Cotton	Wool	Rayon- action	Non- Callul	Grand Lotal
1949-54 1955-60		63.2 66.5	14.6 13.4	18.1 11.4	4.1 8.9	1 <b>00</b> .0
Mon's and boys'	wear					100.0
1949-54 1955-60		<b>24.0</b> 75.6	<b>14.2</b> 13.2	10.0 6.1	1.8 5.1	<b>160.6</b> 1 <b>60.</b> 0
Women's, minees	and junious' wear				2.1	1040.0
1949-54 1955-60		42.4 48.6	16.6 15.9	32.9 20.0	8.1 15.5	1 <b>00</b> .0
Girls', children's	and infants' wear					
1949-54 1955-60		79.1 80.2	9.9 7.4	9.6 7.4	1.4 5.0	100.0 190.0
Home furnishings						
1949-54 1955-60	· · · · · · · · · · · · · · · · · · ·		13.5 10.1	11.5 18.1	1.3 6.1	100.0 100.0
The consumer-type	producta					
1000 00	- 		5.6 4.1	<b>23</b> .3 <b>26.2</b>	0.9 5.0	100.0 100.0
industrial uses						
1949-54 · · · · · · · · · · · · · · · · · · ·	· · · · · · · · · · · · · · · · · · ·	<b>65.0</b> 53.5	2.9 1.0	<b>26</b> .5 27.5	5.6 18.0	1 <b>00.</b> 0
'etci		-		2		100.0
1949-54 1955-60	· · · · · · · · · · · · · · · · · · ·	67.2 63.9	9.9 8.7	19.5 17.8	3.4	1 <b>60</b> .0 1 <b>60</b> .0

Sounce: To.stille Organon, December 1963.

## TABLE II.13. JAPAN CONSUMPTION OF LEXTER PROME BY END-UNIS (Percentage distribution)

	Cutton	Weel	Report	Num- cell abates	Othere	Total
Apparol and household uses						
1953-54 average	49.7	15.4	23.4	1.0	10.5	108.0
1955-	43.0	15.4	23.3	8.1	10.2	100.0
Industrial uses						
1963-1964 average	81.0	1.4	14.0	2.4	0.2	100.0
1955-1960	\$6.0	1.5	23.6	18.7	0.2	300.0
Total						
1963-1954 average	\$2.6	14.1	22.5	1.2	9.4	100.0
1965-1980	44.4	13.9	23.4	9.2	9.1	100.4

Charles : Partiererfer Brende in Consequences / Prostle Aller, Interdictional Cotton A Interry Consection

of the 1950's, by rayon and later in the decade rayon lost ground to nylon. Polyester has entered the field recently competing with nylon and other fibres. In industrial uses other than tyres, synthetics have also been gaining. In Japan, rayon and synthetics recorded net gains, whereas cotton recorded net loss and wool maintained its share of the market. With regards to tyres, similar trends to that of the United States have been observed with a lag of five years; rayon was replacing cotton, and in 1959 synthetic fibres entered the field', competing with both cotton and rayon. Synthetics have also been gradually gaining ground from cotton and hard fibres in the important field of fishing nets and twine.<sup>34</sup>

## III. Synthetic rubber

## PRODUCTION AND GRADE

67. Up until the beginning of the Second World War natural rubber was predominant. As a war emergency effort, the United States Government unitiated a programme for the production of synthetic rubber (SBR) to supplement the then gradually dwindling supply of natural rubber at its disposal. After the war, the position of synthetic rubber was rather precarious since it could

<sup>14</sup> See also: Prospective Trends in Consumption of Textile Fibres, International Cotton Advisory Committee (Washington, March 1962), Agricultural Commodities and Projection for 1970, FAO (Rome, 1952).

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not compete with natural rubber in either quality or in cost. This situation has gradually changed in subsequent years; several improvements have been introduced in the quality of synthetic rubber and cost reductions were realized which, among other things, made it possible for the production of synthetic rubber to grow at a fasten rate (11 per cent per annum since 1950) than natural rubber (about 1 per cent). Consequently the share of synthetic rubber in total rubber production has also been increasing (see figure II<sup>1</sup>) and by 1962 its share exceeded that of natural rubber.

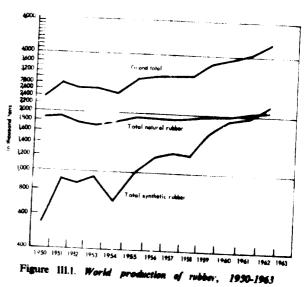


TABLE III.T.	WORLD	PRODUCTION	OF	SYNTHETIC	RUBBER.	1950-1964
		(In thousan	dl	and tomai	,	

19 <b>3</b> 0	1952	1954	/9.56	1944				
					1960	1961	1962	1963
574	873	710	1 <b>,200</b>	1,190	1,596	1,568	1,758	1,81
. 58	74		130				16	2
476	799	623	1,000	135 1,055	160 1,436	164 1,404	166	175 1,60
							- 12 / 1	1,000
					19	50	68	87
•	5	7	11	54	366	788		
						-		507
-	5	7	11	21				97
								106
				_				- 94
		_		11	90			85
							11/	125
534	878	717	1,211	1,244	1,001	3 1 <b>.976</b>	14 2.240	17 2 <b>,430</b>
n.a.	275	7.4				,		4,930
B.8.	56	67	п.н. 72	n.a. 84	410 15	D.a.	n.e.	8.a.
	5'; 58 476 	5 <sup>3</sup> 1 873 58 74 476 799 	5 <sup>1</sup> ; 873 710 5 <sup>8</sup> 74 87 476 799 623 	574       873       710       1,200         58       74       87       120         476       799       623       1,000          5       7       11          5       7       11          5       7       11          5       7       11          5       7       11               534       878       717       1,211         n.a.       275       n.a.       n.4.	511       873       710       1,200       1,190         58       74       87       120       135         476       799       623       1,000       1,055          -       -       -       -         -5       7       11       23          5       7       11       23          -       -       -       11         534       878       717       1,211       1,244         n.a.       275       n.a.       n.a.       n.a.       n.a.	574       873       710       1,200       1,190       1,596         58       74       87       120       135       160         58       74       87       120       135       160         476       799       623       1,000       1,055       1,436            19          5       7       11       23       80          5       7       11       23       80           10       12       12       12           11       20       67       12       12           11       90       135       1400       1,001            11       90       12       12       12           11       90       135       1,001       1,001       1,001         534       878       717       1,211       1,244       1,001       1,001	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$1954$ $1956$ $1958$ $1961$ $1961$ $1962$ $5^{7}$ ; $873$ $710$ $1,200$ $1,190$ $1,596$ $1,568$ $1,758$ $58$ $74$ $87$ $120$ $135$ $160$ $164$ $168$ $476$ $799$ $623$ $1,000$ $1,055$ $1,436$ $1,404$ $1,574$ -       -       -       -       19 $50$ $68$ -       -       -       -       19 $50$ $68$ -       -       -       -       19 $50$ $68$ -       -       -       -       19 $50$ $68$ -       -       -       -       17 $40$ $63$ -       -       -       -       12 $40$ $45$ -       -       -       11 $90$ $106$ $117$ $534$ $878$ $717$ $1,211$ $1,244$ $1,801$ $1,976$ $2,240$ n.a.       275 $n.a.$ $n.a$

Concellural Trade ", Paper presented to United Nations Conference on Trade and Development, 1966. " Spations and their Millers on

68. Excluding centrally planned economies, the United States and Canada (see table 111.1) were for a number of years the only producers of synthetic rubber. Gradualiy, however, other production facilities have been initiated in a number of European countries, including the Federal Republic Germany, Italy, the United Kingdom, France and the Netherlands, Japan, Australia and Brazil. Although the United States has maintained its position as the largest producer of synthetic rubber, its share in world production has been declining from about 90 per cent in 1950 to 66 per cent in 1963, and the Western European

share, in the same period, has increased from zero to 21 per cent.

69. While SBR rubber was the first to be developed, several types of synthetics have since been developed, i.e. butyl, neoprene, N-type, as well as the new types introduced recently, cis-polyisoprene (natural synthetic), cis-polybutadiene and ethylene-propylene rubber As the properties of these synthetics differ, they have been able to fulfil certain needs in specific applications. The volume of production of syn.hetic rubber by types is shown in table III.2 for the United States of America,

France

	t i fanningen a son so annar s	1962			1963
f rubber	U.S.A.	Canada	Pressor	U.S.A.	Canada •
	1 000 Per cent	1 000 Per cent	1000 Bar cant	1000	1000

TAM# 111.2.	<b>PRODUCTION OF</b>	SYNTHETIC	RUBBER	BY TYPES,	1960-1963
-------------	----------------------	-----------	--------	-----------	-----------

	(1 <b>00</b>   (1 <b>01)</b>	Per cent	1 000 Netta	Per cent	1 000 tens	Per cent	1 000 Ione	Per cent	1 000 Manua	Per cent	1 000 Ions	Per cent
S-type	1,1 <b>94</b> 1 <b>29</b>	75.9 8.2	111	66.1	36	<b>54</b> .5	1,159	72.1 8.0	123	69.2	55	57.2
Dutyl	46	5.7 2.9	29	17.2	<b>22</b> 3	33.4 4.5	108	6.7 3.0	31	17.3	24 8	<b>25</b> .0 <b>8.4</b>
Stereo regular	93 23	5.9 1.4	28	16.7	5 b	7.6	140 25	8.7 1.5	24	13.5	 9 b	9.4
GRAND TOTAL	1,574	100.0	168	100.0	66	100.0	1,608	100.0	178	100.0	96	100.0

SOURCE: Prenor : Commission de la Chimie, 4º Plan de Modernisation, Groupe des Caoutchouse Synthétiques et Noirs de Carbone (mai 1963). Canade and USA : Rubber Statistical Builletin, Secretariat of the International Rubber Study Group, London. — = nil.

Type of

· Estimate based on Jan/Nov.

Polybutadiene.

#### TABLE 111.3. EXPORT OF SYNTHETIC RUBBER, 1950-1964

#### (In thousand long tons)

	1950	1952	1954	19 <b>5</b> 6	1 <b>95</b> 0	1960	1691	1962	196
America									
Canada	39 8	43 22	60 30	80 149	49 193	106 342	117 297	119 304	122 283
Asta									<b>44</b> 5
Japan	_	-	_				5	6	8
Europe							-	-	•
Press				_		6	10	24	41
Italy.	-	(0.3)	(0.9)	2	5	21	18	24	39
Netherlands.			—		(0.6)	36	45	41	51
United Kingdom	_	-	_		(0.7)	6 20	22 21	40 28	61 34
Total (assisting controlly planned economics)	47	65	91	231	259	540	536	586	639
Controlly planned oconomics									
Bast-Germany.		27	37	<b>39</b>	47	49	43	45	<b>n.e</b> .
Poland.					-	9	10	10	<b>D.6</b> .
	8.4.	8.4.	B.4.	23	42	32	38	32	8.8.

Bernens: Ander Statistical Belleth, Bereinstat of the International Rubber Study Group, London, FAO, " Groubstics and Their Miless on Agricultural Trade ", paper presented at the United National Conference on Trade and Development, Geneva, 1964.

TABLE 111.4.	NET	TRADE	IN	SYNTHETIC	RUBBER	BY	MAJOR	EXPORTING	COUNTRIES,	1950-1964
				(1	Export-In	npo	rt)		•	

and the second s	1 <b>93</b> 0	1952	1954	1956		1960	1961	1962	/96.)
America									
Canada United States Asia Japan			+ 13	it≊ 1 <b>42</b>	+ 87 + 184 17	+ 333	+ 285	+ 290	
Europe France Germany (Fed. Rep. of) Italy Netherlands United Kingdom			13 10 11	35 24 15 3	58 35	84 28	58	43 39 + 6 + 30 22	

SOURCE: Computation based on table III.3 and "Rubber Statistical Bulletin".

TABLE 111.5. EXPORT OF SYNTHETIC RUBBER BY TYPES, 1962-1964 (In thousand tons)

Type of rubber	1962		1963	19
and a second second second second second second second second second second second second second second second	United States of America	Prance	United States of America	Prance
I-type Jutyl N-type Neoprene Mareo regular	197 27 9 70	4 12 (5)	176 33 8 65	1  3  3
Rhers GRAND TOTAL		41		8 •

SOURCE: France : Commission de la chimie, Groupe des caoutchouce synthétiques et noire de carbone (mai 1963). Others : Rubber Statistical Bulletin, International Rubber Study Group, London.

Canada and France. The figures indicate that the S-type rubber predominates.

70. With respect to centrally planned countries, available data on synthetic rubber production are scanty (see Table III.1). Besides Eastern Germany, the USSR (both of which have production facilities dating prior to the Second World War) and Poland, synthetic rubber is also being produced in China (mainland), Romania and Czechoslovakia.

71. The export of synthetic rubber has been increasing by about 20 per cent annually from 47,000 tons to 640,000 tons in the years 1950 and 1963 respectively, the only exporting countries, excluding centrally planned countries, as indicated in table 111.3, for a number of years have been Canada and the United States of America, and in recent years, a number of European countries and Japan have entered the export market, sharing in 1962 about 37 per cent of the total world market.

The same countries are also the major importers, sharing over 50 per cent of the export market. In centrally planned countries, the trade in synthetic rubber is primarily regional in character.\*

72. In terms of net trade (export minus import), the United States of America and Canada heve been net exporting countries and only since 1960 and 1961 have Italy and the Netherlands respectively attained net exporting positions. The other major exporting countries are net importers (see table 111.4).

73. With respect to types of exported synthetic rubber, data for the United States and France are given in table III.5. They indicate that, for France, rubber other than S-type predominates on the export market, comprising in 1962-1963 about 70-85 per cent of its export.

<sup>&</sup>lt;sup>10</sup> FAO, Synthetics and Their Effects on Agricultural Trade uper pre-united to the United Nations Conference on Trade and levelopment, Geneva, 1964. sence on Trade and

TANK BUCK OF INTIMIC NUMBER IN DEFENSION, 1963

7	770	4		ł	J	(22)	1		ł		1	
*/  /  	-	12	1	12		1	L. <b>H</b>	1		8	1	8
	71 WK		-	,		ç	ŝ	2				
		35	•	I		, ( ; ;		•		3		
		2	I	1		71	R	0.0	<b>86</b> 5,1	16.1	91 <b>9</b> ,1C	124
	120,512	45.7	20,654	60.7	27,006		108,62	56.9	271	3.3	ACE. 705	1.64
	<b>260,23</b>	1.00	13,978	41.1	13,400		23,172	<b>1#</b>	139	1.7	137,789	33.1
Outside pleased economics	2,355	3	APPLE	211.5			17,783	94.0	1,967	23.9	31,509	7.6
	8,003	3.1		3	*		I	1	2.58	31.1	166,61	32
	51,976	12	£	2	537		1	I	1,232	14.8	53,710	12.9
	12,822	3	Ş	<b>*</b> 1	531		¥	0.9	-	0.1	14,467	3.5
	2,988	011	1	1	5		175	0.3	7	1	3,908	8.U
	X)	<b>L1</b>	3	9.61	1,917	64	3,767	7.2	2	10.7	0647/1	4
Terr	789/582		LANK	9	39,006	,	52,336	989	116.8	100.0	416,789	100.0
		and the second se										

Bruch Mite Battel Mith (Heat 1948

	1930	1952	1936	19 <b>58</b>	1960	1961	1962	1963	1964
America									
Canada United States of America	67 2	58 3	67 14	73 18	68 24	71 21	71 19	68	
Asia						41	19	18	
Japan	-					10	9	9	
France Germany (Fed. Rep. of) Italy Netherlands United Kingdom		6	18	<b>22</b> 3 6	35 25 54 50 22	25 21 54 55 20	38 27 47 90 24	42 37 54 72 27	

TABLE III.7. SHARE OF EXPORT OF SYNTHETIC RUBBER IN TOTAL PRODUCTION, 1950-1964 • (In percentage)

· Calculation based on tables III.1 and III.3.

74. Direction of export from the major exporters indicate that Western Europe imported half of the total export from these countries, followed next by Asia and Latin America (table III.6). With respect to individual countries, most of the United States export, next to Europe, goes to Asia and Latin America. Countries of centrally planned economies are major importers from the United Kingdom, the Federal Republic of Germany, Italy and Japan. Half of the export from Japan went to Oceania and Asia, and most of the rest to centrally planned economies and Latin Americe.

75. Since 1950, export has increased at a faster rate than production. Its share in total production increased from about 9 per cent in 1950 to 26 per cent in 1963. The share of export in local production of the major exporting countries is given in table III.7. The highest ratios are for the Netherlands and Canada; for most of the remaining countries, the ratio has in recent years been about 20 per cent or more. The share of exported synthetic rubber by types in total production (see table III.8) for the United States and France indicates a relatively higher ratio for butyl, N-type, neoprene and other specialized synthetic rubber as compared to the S-type.

TABLE III.8. EXPORT OF SYNTHETIC RUBBER BY TYPES, 1962, 1963 (Percentage of local production)

	ħ	<b>9</b> 4	-	, u		æ					United of A	States merica	In	Nor
	 										1962	1963	1962	1963
-type.		•									18	15		
THE PLAN											30	30	11 55	20 54
i-type there *											20	17	17	38
	·	•	·	•	•	•	•	•	·	•	29	22	80	90

Sounce: Tables III.2 and III.5.

. For United States of America in

ad others; France, polyinstadione

#### CONSUMPTION

76. Similarly, world consumption of synthetic rubber has been growing at a fast rate; as indicated in table III.9, it has increased from about 600 thousand tons in 1950 to 2.3 million tons in 1963. Here again, the United States' share in total consumption has declined from 93 per cent in 1950 to 56 per cent in 1963, whereas the western European countries' share has increased from 3 to 26 per cent for the same years respectively, and the rest of the world also saw an increase in their share of total consumption.

77. Besides the various factors that affect the consumption of rubber in general, the growth in the consumption of synthetic rubber is attributed primarily to the net gain, over the years, from natural rubber.

78. As table III.10 indicates, the slare of synthetics in total rubber consumption has been increasing and by 1962 it had reached about half of the world total. This ratio, however, differs from one country to another; the United States and Canada, forming the upper boundary, have 68 to 73 per cent, and the lowest ratios are obtained in China and India.

79. Furthermore, the synthetic rubber family offers, besides the SBR, a variety of types — the number of which has been increasing over the years — that have special properties catering for specific applications and have also contributed to the net gain in the use of synthetic rubber. Examples are the recently introduced new rubber, cispolysoprene, the practically chemical duplicate of natural rubber, cis-polybutadiene, and ethylene-propylene rubber.

80. Mention may also be made at this point of several important advantages of synthetic rubber that have played an important role in their growing use. First, synthetic rubber has a more defined level of uniformity and purity; this is an important advantage for small users of rubber lacking access to testing facilities and laboratories. In this connexion, synthetic manufacturers have been actively encouraging the use of synthetic

	1950	1952	1954	1956	19.58	1989	1962	1962	1963
America									
Canada	23	34	30	48	47	56	63	73	84
United States of America	538	807	637	1 874	2 880	16 1,079	20 1,1 <b>02</b>	28 1,256	3- 1,30
SUB-TOTAL	<b>56</b> 1	841	667	923	929	1,151	1,185	1,357	-
Asie							1,105	1,337	1,421
Chine (Taiwan)					1	16	13		
India				2	3	6		10	-11
Japan			2	,	17	61	Ň	104	125
SUB-TOTAL	_			11	21	83	106	114	13
Europe (western)						•5	100	1 14	134
France.	7	11	14	32	55	91	*	108	123
Germany (Fed. Rep. of)	3	10	17	36	54	104	120	129	141
Italy •		7	10	15	28	58	65	73	
Notherlands.			1	3	5	12	ij	14	15
United Kingdom	3	5	9	41	65	116	121	128	139
Other, Europe	5	6	8	27	35	64	72	91	103
SUB-INTAL	18	39	59	154	252	445	487	543	61 1
waralis	-		1	11	17	25	23	25	33
the countrise		3	10	34	45	78	81	99	
GRAND TOTAL	579		730					**	<b>7</b>
CHAND TUTAL	3/9	863	739	1,133	1,254	1,782	1 <b>,882</b>	2,128	2,305

# TABLE III.9. WORLD SYNTHETIC RUBBER CONSUMPTION, \$1930-1963 (In these and long tons)

Bounce: Statistical Bullerin, International Rubber Study Group, London.

\* 1930 Agures included in "Other, Europe". \* Netimote.

# TABLE III.10. WORLD RUBBER CONSUMPTION, 1950-1964 (Percentage synthetic use)

	1969	/962	1954	1996	1950	1960	1 <b>961</b>	1962	1963
America									
Canada	33.3	58.8	41.7	52.8	36.0	61.5	67.0	67.6	
Branii	_			2.7	4.6	27.1	33.9	41.8	
United States of America.	42.8	64.0	51.6	60.9	64.5	<b>Ø</b> .3	72.1	73.1	
Anin .									
Chine (Taiwan)			_		1.0	11.8	13.4		
India			_	6.5	7.9	11.5	15.8		
Japan		-	2.2	7.6	11.7	27.0	32.3	16.4 35.4	
Europe (western)					••••		- <b>4</b> . J	33.4	
Press	6.4	8.3	9.9	19.3	28.7	41.7	43.1	46.4	
Germany (Rep. Pod. of)	3.7	9.7	11.6	21.2	29.4	41.6	46.9	46.9	
		15.6	15.6	21.4	33.3	43.4	44.8	47.7	
Notherlands.			5.0	13.0	21.7	37.5	39.4	41.2	
United Kingdom	14	2.5	3.5	17.0	26.3	38.3	41.1		
Other, Burepe.	2.4	6.7	6.7	20.2	22.6	35.0		44.0	
			•••			33.0	36.9	41.2	
		~~	2.2	22.5	32.7	48.3	44.2	42.4	
Mine countries 4	-	3.4	63	28.2	22.4	13.5	38.0	36.5	
GRADE TOTAL	25.2	37.4	-						
	<b>67.6</b>	37.6	<b>29.</b> A	31.1	38.4	46.54	<b>41.A</b>	48.5	

n Association Inc., Bubber Industry Ports, 1965. nts: United States Rubber Mer

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rubbers by offering technical assistance to rubber manufacturers.

81. In connexion with rubber consumption (synthetic and natural), per capita income is the important explanatory variable. For a sample of 34 countries regression analyses were performed yielding a coefficient of determination of 0.87. The average relationship between per capita consumption and per capita income is defined by the following logarithmic formula:

$$Y = .00224 x^{1.07990}$$

The income elasticity coefficient implies that, on an average, a slightly higher percentage change in per capito rubber consumption is associated with an equivalent percentage change in per capita income. Other factors affecting rubber consumption include technological development in tyre production such as tubeless tyres, longer tyre life and small size tyres, as well as changes in the ratio of replacement tyres to tyres for new vehicles.

82. With respect to future trends, the Food and Agriculture Organization of the United Nations estimated that total world rubber consumption, excluding that of centrally planned countries, might increase from an average of 2.93 million tons for 1957-1959 to between 4.94 to 5.74 million tons in 1970.

#### WORLD RUBBER CONSUMPTION, 1970 (Million metric tons)

											Low	Niek
United States of Americ	9											
Germany (Fed Ban of)	•	•	4	•	•	•	•	•	٠	•	2.15	2.53
Germany (Fed. Rep. of) France	• •	·		·	·	٠	·	•		•	0.41	0.46
France . Other FFC Countries	• •	•	,	·	·	٠	·	•	·		0.37	0.42
Other EEC Countries.	• •	•	·	·	·	·	·				0.27	0.29
United Kingdom.	• •	·	·	·	÷	·	٠		•		0.36	0.41
Other economically advan	CBC	C	)UI	ntr	ie	•	•				0.88	1.06
Other countries	• •	·	·	٠	•	·	•				0.50	0.57

SOURCE: FAO, Agricultural Commodilies Projection for 1976 (Rome, 1962).

TOTAL 4.94

5.74

Other western Europe (excl. Mediterranean countries), Japan, Canada, Australia, South Africa.

83. Based on these projections and assuming a contimesed increase in the share of synthetics in total rubber consumption in the major consuming countries, the increase in world consumption of synthetic rubber may be estimated at an average of from 0.90 million tons for the years 1957-1959 to between 2.67 million to 2.84 million ia 1970.

SYNTHETHC	RUDDER	CONSUMPTION,	1970	<b>NUTIMATES</b>
	( <b>in m</b>	illon metric ioni	)	

-

	Low	Migh
United Satates of America	1.61	1.90
United Kingdom	.58	.58
		.22
Other consuming countries	.24	.46 .34
-		

TOTAL

3.00

84. The above estimates were based on the assumption that the share of synthetic rubber in the major consuming centres will increase to between 73 and 75 per cent in the United States and to between 50 and 55 per cent for Western Europe, Australia and South Africa, Argentina, Brazil and Mexico.30

85. These estimates exclude centrally planned countries. Data were made available by Hungary and Yugoslavia on estimates of production and consumption in 1970 and 1975.17

	1970	ı	975
Hungary	Consumption	Production and sone)	Communition
Synthetic rubber.	 18-20 18-21		
Yugoslavia			
Synthetic rubber Natural rubber	 23 34	.30 	30 46

#### END-USES FOR RUBBER

86. The end-uses of rubber for France, Japan, the United Kingdom and the United States indicate that tyre and tyre products consume about 50 per cent and over of total consumption (table 111.11). In the United States, where passenger cars have a comparatively more predominant position on the economy of the country, the share of this category is higher, averaging about 62 per cent. Data for a number of developing countries (see table 111.12) indicate that the share of tyre and tubes in total rubber consumption ranged between 70 and 90 per cent.

87. With respect to the share of synthetic rubber, it has been increasing in each of the main end-uses for the above countries (table 111.13). The use of synthetic vs. natural rubber differs from country to country and in different applications, depending on economic and technical considerations, and on the availability on the domestic market of sufficient supplies of natural or synthetic rubber. In certain applications where specific characteristics of synthetic or natural rubber are required, cost consideration may be given secondary importance. In others, cost consideration, separately or in combinetion with technological or property requirement, are determining factors.

ss. A number of important properties of SBR synthetic and natural rubber have been compared in figures III.2 and III.3. Three of these properties are considered important factors for processing in tyre factories: mixing, raw tack and fast curing; the rest are considered important for judging performance. SBR is said to be superior to natural rubber in wear resistance, groove crack resistance, aging resistance, and fast curing; its major drawback is high heat build-up. The superiority

" These are not officially approved plan target figs

3.41

<sup>&</sup>lt;sup>10</sup> See also: FAO, Agricultural Commodities Projection for 1990 Lonne, 1962). (Ba

		France	Nothington a se	Ja	<b>jen</b>	U	nited King	dom	United	States of .	Imerica
	1936	1961	1962	1961	1962	1956	1961	1962	1936	1961	1962
"yre and tyre products											
Passenger cars	<b>48</b> . j	<b>46</b> .9	47.1	6.5 26.9	6.9 26.8	15.6 22.9	16.4 19.4	18.2 18.4			
	3.8	3.0	3.0	3.2	2.6	2.2	1.3	1.3			
Tubes	4.3	3.8	3.6	3.3	4.8	4.3	3.9	3.7			
Other tyre products	3.3	4.0	3.3	5.9	5.5	9.3	12.2	12.8			
SUB-TOTAL PER CENT	59.5	57.7	57.0	45.8	46.7	54.3	53.2	54.5	62.4	63.3	62
SUB-TOTAL IN 1,000 TONS	<b>98.9</b>	128.5	133.2	1 19.0	134.8	126.1	! 52.8	158.3	897.0	957.5	1.066
on-tyre products											•
Belting	2.6	2.5	2.5	5.4	5.2	2.6	2.5	2.3	_	_	
Cables	3.6	4.7	4.5	4.0	2.8	4.1	2.9	2.3	3.3	2.3	
Footwear.	9.7	10.5	10.1	18.0	17.9	10.5	5.8	5.7	5.6	5.8	
Cellular products	7.9	9.3	9.8	7.3	7.6	6.6	5.1	5.2	9.8	9.9	
Other non-tyre products	16.8	15.3	16.2	19.5	19.8	21.9	30.5	29.9	19.0	18.7	
SUB-TOTAL PER CENT	40.5	42.3	43.0	54.2	53.3	45.7	46.8	45.5	37.6	36.7	37.
SUB-TOTAL IN 1,000 TONS	67.4	94.0	100.2	140.8	159.5	106.2	134.6	132.2	539.5	572.0	652
TOTAL PER CENT	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100
TOTAL IN 1,000 TONS	166.3	222.5	233.4	259.8	294.3	232.3	287.4	290.4	1.436.5	1.529.5	1,718

## TABLE III.11. CONSUMPTION OF RUBBER BY MAIN END-USES - SELECTED COUNTRIES (Percentage)

Sounce: Rubber Statistical Bulletin, London.

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#### TABLE 111.12. SHARE OF TYRES AND TUBER IN TOTAL RUBBER CONSUMPTION LATIN AMERICA

					¢			,										Personage of issue
Argentina.																		83
Dreall	•	•	•				•	•		•								85
Colombia.	•	•	•	•	•	•	•	•	•	•	•		•		•	•		70
Mentice.																		92
																		80
Venanuela.	٠	•	٠	٠	•	•	•	•	٠	•	•	•	•	•	•		•	75

Sounce: BCI.A, La Industria Quindos on America Latina, vol. 1 (1962).

of SBR in the above four important properties have been primarily responsible for the gain in the use of this synthetic in a number of applications, most important among which is that of passenger car tyres. On the other hand, the high heat build-up, while of minor importance in passenger tyres, is considered an important handicap in use for heavy service tyres.<sup>26</sup>

<sup>10</sup> The Future of Natural and Symbotic Rubbers, The International Rubber Study Group., Brettenham House, London.

TABLE III.13. PERCENTAGE OF THE SYNTHETICS IN TOTAL RUBBER CONSUMPTION, MAIN END-USE

		Preser			<b>Fill</b>	u	abod King.	lam -	U	inted State	1
	1996	1961	1962	1961	1962	1936	1961	1962	1956	1961	1963
Tyree and tyre products											
Presentation and a second seco	13.0	36.0		-	65.5	36.6	65.8	70.2			
Commercial vehicles					25.8	9.5	22.6	18.8			
<b>Cyde</b>	5.7	28.2	_	13.1	15.2	3.7	38.4	44.4			
<b>Tube:</b>	98,1	<b>99.4</b>	-		66.1	58.4	84.8	86.0			
Other type products	11.0	33.6	-	10.9	36.2	17.8	58.6	<b>59.</b> 1			
Toral Non-lyve produce	18.5	39.6	-	-	36.5	22.3	49.2	58.8	<b>59</b> .A	71.0	<b>71</b> .4
Belling	12.7	30.2		24.1	30.8	12.8	19.8	28.1			
Califes	30.7	79.1		63.3	61.6	16.7	45.8	44.7			
Fedhuer	11.9	<b>67.5</b>	_	32.5	33.6	84	44.4	4.7			
Colletter products.	23.5	38.6	-	38.0	33.0		31.1	31.6			
Other son-lyse products	21.1	32.3		<u></u>	34.4	11.6	33.0	34.8			
Torne.	19.7	47,5		H.I	36.5	18.7	34.3	35.9	8.3	73.9	75.0

Sounce: Robber Statistical Bullotin, London.

TABLE III.15. UNITED KINGDOM, RUBBER CONSUMPTION IN TYRE AND TYRE PRODUCTS, 1962 (Pounds per tyre or tube)

Tyre and tyre products	Grand total	Naturai rubber	Synthelic Tubber	S-type	Butyl	Other
			1 40047	Percenta		synthetic synthetic
Car Commercial vehicles Tractor, earthmover and land/road Motorcycles, bicycles and scoolers All others Tubes (all types)	8.5 41.0 36.9 0.68 8.8 1.3	2.5 33.3 12.5 0.38 6.5 0.2	6.0 7.7 24.4 0.30 2.3 1.1	92.2 86.9 98.5 100.0 100.0	0.5 0.5 0.15	7.3 12.6 1.3

SOURCE: Rubber Statistical Bulletin (February 1964), International Rubber Study Group, London.

89. The data for Japan and the United Kingdom indicate the rather high percentage of synthetics used in tyres for passenger 'cars (see tables III.13 and III.15). In contrast, in France, the use of synthetic rubber in tyres for passenger cars and commercial vehicles is lagging behind the use in Japan and the United Kingdom.

90. With respect to the use of the synthetic family, with the exception of tubes, for which butyl is the dominant rubber, the S-type predominates in all the main uses and the remaining types of rubber play a rather marginal role (tables III.14 and III.15).

91. As for consumption of rubber per tyre, the data for the United Kingdom indicate that in 1962 about 3.86 kg. were used in passenger car tyres and 18.64 kg. for commercial vehicles. On the other hand, in the United States of America the 1958 census of manufactures indicates an average of 4.13 kg. and 19.65 kg. per tyre for passenger cars and commercial vehicles respectively, and the average consumption for more recent years is lower than these figures.

TABLE III.14. RUBBER CONSUMPTION BY TYPE IN TWO MAIN END-USES,

(Percentage distribution)

	Type and	lyre products	Nen-tyre	products
	United States of America	United Kingdom +	United States of America	United Kingdom
Natural.	28.6	48.4		
Synthetic		47.8	24.2	63.4
S-type	· 71.4	52.2	75.8	36.6
Butyi	61.2	43.2	50.0	50.0
Neoperation	· <b>4.4</b>	6.2	3.2	
Neoprene	· 0.5	n.a.		
N-type	. •		13.0	
		n.a.	5.5	
Others		ñ.g.	1.5	
• • • •	0.1	2.8	2.5	
Тотл	L 100.0	100.0	100.0	

Rubber Statistical Bulletin, International Rubber Study ne (Foloryary first half ye ar of 1963. Data for noti-tyre products are

d in others

## IV. Nitrogenous fertilizers

## PRODUCTION AND TRADE

92. In the last decade, world output of nitrogenous fertilizers have been increasing at the rate of about 8 per cent per annum, from 4.4 million tons in 1951 to 12.8 million tons in 1962. Western Europe produced about 40 per cent of world output and North America averaged one third. The next major producers are centrally planned countries and Asia (principally Japan). The total share of developing countries in world output averaged about 6 to 7 per cent (see table IV.1).

93. With respect to types of fertilizers produced, ammonium nitrate and ammonium sulphate comprise about half of the total. The latter type of fertilizer along with ammonium sulphate nitrate, sodium nitrate, calcium nitrate and calcium cyanamide have decreased their share of total output, whereas urea, and complex fertilizers have been increasing their share. The share of other nitrogenous fertilizers has also been increasing. This class of fertilizers, which are used primarily in the United States include anhydrous ammonia, aqua ammonia, and ammonium-nitrate-water solution, a combination of ammonia, ammonium nitrate and urea dissolved in

94. The annual rate of growth of trade has kept pace with the total production and in the last decade exports comprised about 25-30 per cent of the total output. Western Europe was the major exporter, sharing over 60 per cent of the total, followed next by North America. Asia (Japan) has been increasing its share from 7 per cent in 1953 to 13 per cent in 1962, whereas the share of South America, (Chile), has been decreasing from 17 to 6 per cent for the same period (see table IV.3). On the import side, Western Europe, North America and Asia are the major importing countries; Asia's share in total import has been increasing, while North and Latin America and the Middle East recorded a decrease. As for the balance of trade, measured in terms of export minus import, Western Europe is the major net exporter of nitrogenous fertilizers, and centrally plauned economies have also been minor exporters. The remaining regions of the world were net importers, Asia being the principal

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TAKE IV.1. WORLD PRODUCTION OF NETHODINGS PRINLINGS

(In Amural mode nue, N)

1906/1906

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		3083358222		<u>*</u>		<u> </u>		25557 25557 2557 2557 255 255 255 255 25		<b>4</b> 334559333	4 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	<b>8</b> .51 <b>8</b> 4 1 5 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6		<b>36.1</b> <b>26.2</b> <b>26.2</b> <b>26.2</b> <b>27.2</b> <b>26.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.2</b> <b>27.22222222222222</b>		X52955313
Marc Gand	\$	Ĩ	1975	2	7,182	Ĩ	1951	9	9,710		10,730		<b>1</b> , <b>7</b>	N <b>90</b> .0	12,760	I

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## TABLE IV.2. TYPES OF NITROGENOUS FERTILIZERS MANUFACTURED IN THE WORLD, 1954/55 - 1959/60 (Percentage of total)

	1954-55	1955-56	19 <b>56-5</b> 7	1957- <b>58</b>	1958-39	1959-60
Ammonium sulphate	31.2	31.6	30.0			
Ammonium nitrate				<b>28</b> .7	28.5	26.0
Ammonium sulphate nitrate, sodium nitrate	25.2	24.8	23.9	24.6	23.6	24.8
calcium nitrate and calcium cyanamide Complex fertilizer	16.6	14.2	14.8	14.3	12.1	11.1
Line	5.1	6.0	7.9	8.1	8.7	9.5
Urea	2.3	2.8	4.7	5.1		
Other nitrogenous fertilizers	19.6		••••		6.2	6.4
	19.0	<b>2</b> 0.7	18.8	19.1	21.0	22.3
Тота	100.0	100.0	100.0	100.0	100.0	100.0

SOURCE: FAO, Fertilizers : An Annual Review of World Production, Consumption and Trade.

Continents	19.	55/1954	19.	\$5/1956	19.	17/1958	19	<b>59/196</b> 0		
	Tous	Per cont	Teas	Per cent	Tonu	Per cent	Tens			61/1962
							1000	Per cent	Tons	Per ce
<u> </u>				Exports						
Western Europe	838	58.2	853	62.2						
Contrally planned economies	<b>£</b> 1	3.5	113	52.2	1,364	58.1	1,622	60.1	1,800	58,8
North America	206	14.3	412	6.6	115	4.9	187	6.9	233	7.6
Letin America	238	16.5	166	24.1	382	16.3	348	12.9	427	13.9
(Chile)	(238)	10.5		9.7	231	9.8	199	7.4	194	6.3
	107	7.4	(161)		(229)		(197)		(194)	0, 3
(Japan)	(107)	1.4	126	7.4	256	10.9	340	12.6	404	
NTICE			(126)		(255)		(340)		(396)	13.2
Doeania.	_						-		4	•••
diddle East							4	0.1		0.1
WORLD TOTAL	i,440	100.0	1,710	100.0	2,348	100.0	2,700	100.0	3,062	
•				IMPORTS						
Autorn Europe	486	33.7	<b>54</b> 3	•• •						
WIRE THE DESIGN ACODOMICS	n.a.	D.a.		31.0	620	32.0	783	34.4	787	11.0
orth America	414	28.7	n.a. 417	n.a.	57	2.9	97	4.2	78	31.2
tin America.	106	7.3	182	23.8	424	21.9	438	19.3	502	3.1
	273	18.9	413	10,4	123	6.3	143	6.3	134	19.9
rica — Total	54	3.7	413 72	23.6	470	24.2	615	27.0	774	5.3
(South Africa)	(n.a.)	(n.a.)		4.1	86	4.4	99	4.4	122	30.7
	5	0.3	(18)	-	(14)		(23)		144	4.8
iddle East	105	7.3	7	0.4	15	0.8	9	0.4	17	
		1.5	117	6.7	145	7.5	91	4.0	107	0.7
WORLD TOTAL	1,443	100.0	1,751	100.0	1,940	100 0	-		10/	4.2
					1,240	100.0	2,275	100.0	2.521	100.0

TABLE IV.3. INTERNATIONAL TRADE IN NITROGENOUS FERTILIZERS, 1953/54-1961/62 (1,000 metric tons and percentages)

SOURCE: FAO, Fertilisers an Annual Review of World Production, Consumption and Trade. N.a. -- Not available.

95. With respect to the types of nitrogenous fertilizers entering trade, ammonium sulphate and ammonium nitrate are the major fertilizers exported, comprising about 60 per cent of the total. The share in trade of urea, complex fertilizers and other nitrogen fertilizers recorded an increase while the remaining types showed a decrease

in their share (table IV.4). Comparing the share of export in production for the important types of fertilizers; over one third of ammonium suppase, urea, ammonium suppase nitrates, sodium nitrate, calcium nitrate and calcium cyanamide, and about one fourth of ammonium nitrates and complex fertilizers are exported (table IV.5).

### TABLE IV.4. WORLD EXPORTS OF NITROGENOUS FERTILIZERS BY KIND

		1953/1	954	1958 1	939	1959-1	96()	1961 1962		
a management a submany of the second s		Tons	Per ceni	Toms	Per vent	Tons	Per ceni	Tons	Per ceni	
Ammonium sulphate		488,677	39.4	839,383	39.8	892,160	39.7	948,000	14 7	
Ammonium nitrates Ammonium sulphate nitrates		250,417	20.2	406,038	19.3	464,796	20.7	509,000	34.7 18.6	
Sodium nitrate		239,374	* 19.3	96,231 179,456	4.6	120,150	53	141,000	5.2	
Calcium nitrate		171,603	13.8	189,366	8.5 9.0	97,208 207.001	4.3 9.2	179,000 208.000	6.5 7.6	
Calcium cyanamide.	• • •	17,291	1.4	14,748	0.7	3,875	0.2	2,000	0.1	
Aher nitrogenous fertilizers	an an an an an an an an an an an an an a	18.412	1.5	173,132 50,620	8.2 2.4	208,177 90,220	9.3	462,000	16.9	
Complex fertilizers		53,717	4.3	160,152	7.6	90,220 165,149	4.0 7.3	59,000 225.000	2.2 8.2	
T	DTAL <sup>b</sup>	1,239,491	100.0	2,109,126	100.0	2,248,736	100.0	2,733,000	100.0	

(Metric tons N and percentages)

SOURCE: FAO, Fertilizers An Annual Review of World Production, Consumption and Trode.

Included in other nitrogen fertilizers.

The years 1958/59 and 1959/60 include the USSR but exclude other centrally planned countries.

#### CONSUMPTION

96. With respect to the consumption of nitrogenous fertilizers. Western Europe and North America shared about 60 per cent of the total, followed next by centrally planned countries and Asia. The share of Western Europe in total consumption decreased slightly while that of centally planned countries increased. Developing countries alone shared on the average about 15 per cent of the world total consumption (table IV.6). Comparing consumption by major categories of commercial fertilizers, the rate of growth of nitrogenous fertilizers has been increasing, since the post war period, at a faster rate (8.4 per cent per annum) than potash fertilizers (7.6 per cent) and phosphate fertilizers (4.9 per cent). Consequently, the share of nitrogenous fertilizers in total chemical fertilizers has increased and that of phosphate has decreased, and in recent years the three major categories shared the market more or less equally.

#### TABLE IV.5. WORLD EXPORTS OF NITROGENOUS PERTILIZERS BY KIND (Percentage of total production)

	1938-39	19 <b>39-6</b> 0
Ammonium sulphate	33.6	37.0
Ammonium nitrates	19.6	20.2
Urea	31.8	35.0
Ammonium sulphate nitrates, sodium ni-		
trate, calcium nitrate, calcium cyanamide	45.2	41.6
Complex furtilizers.	21.0	18.7
Other nitrogenous fertilizers	2.7	4.5
WORLD TOTAL	24.0	24.2

Source: Computation based on tables IV. 2 and IV. 4.

· Including the UBBR but excluding other controlly plans

While this is true with respect to the world average, the situation differs in each region, the Middle East maintaining the high share of about 73 per cent and Oceania recording a low share of about 3 to 4 per cent (table IV.7).

97. The maldistribution in consumption is also reflected in the use of nitrogenous fertilizers, measured in terms of arable land; Europe consumes about 24 tons per 1,000 hectares of arable land followed next by North America (10.5 tons), Asia (4.1 tons), USSR (3.1 tons) and the remaining regions consume between 1.2 and 2 tons per 1,000 hectares.

98. The relationship between national average crop yield and national average use of the various types of fertilizers per hectare has been dealt with in a paper on fertilizers and economic development.<sup>29</sup> This relationship is illustrated for forty-one countries in figure IV.1. The data yielded a coefficient of determination (R<sup>a</sup>) of 0.83 Using a deviation of one standard error of estimate (illustrated on the chart by the two dotted lines), thirty-one out of the forty-one countries have fallen within these upper and lower limits. The relationship between the increase in crops yield and the increase in application of fertilizers, as reflected in the figure, should be put in the right perspective namely that fertilizers contribute importantly to the increase in productivity. However other factors are also responsible individually and in combination for increased productivity; these factors include the use of improved crops, the introduction of modern practices in irrigation and crop management, etc.<sup>29</sup>

99. Further, the data indicate that, with a few exceptions, most of the developing countries, in the sample, consume less than 25 kilograms per hectare and that a great expansion in the agricultural output beyond a

<sup>&</sup>lt;sup>10</sup> F. W. Parker, "Pertilizers and Economic Development", paper delivered at the Pertilizer Workshop, American Society of Sell Belence, Parene University, Pebruary 12-13, 1962.

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# TABLE IV.7. THE SHARE OF NITROGENOUS PERTILIZERS IN TOTAL COMMERCIAL PERTILIZERS BY REGIONS, 1951-1962

(Percentage of total commercial fertilizers)

	1951-52	1955-56	19 <b>58-5</b> 9	1960-61	1961-62
	26.5	32.2	30.3	31.7	
Centrally planned economies	29.3	32.8	30.3	31.7	32.5
North and Central Americas	27.4	34.2	36.2	39.0	34.5
South America	36.6	42.9	35.9	38.9	40.0 32.8
Asia a la	56.4	52.5	53.2	52.0	53.7
Africa	. 18.4	20.6	25.0	29.5	30.6
Doeania	. 3.9	3.8	5.3	3.3	4.2
Middle East		<b>72</b> .7	78.1	73.0	73.2
WORLD TOTAL	29.1	34.1	33.9	35.8	36.7

SOURCE: Computation based on data from FAO, Production Yearbook 1951-1962.

certain level of crop yield would have to be associated, inter alia, with an increasing use of fertilizers.<sup>30</sup>

100. An estimate of future requirements for fertilizers indicated an order of magnitude for potential world demand in 1980 of about 70 million tons compared to about 27 million tons in 1959/60. Developing countries alone would increase their requirement from about 4 million tons in 1959/60 to 30 million tons in 1980.

101. These estimates were computed for each country in the region, assuming certain targets for food supply

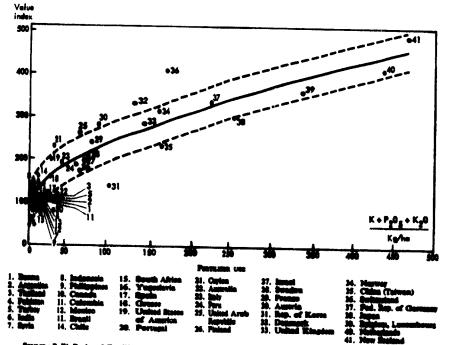
<sup>10</sup> *Ibid.* It was suggested that the use of fertilizers would be essential in order to increase crop yield above 800 to 1,200 kilos of grain per hectare. These levels of crop yield were also considered to equal those of advanced countries at the "take off" stage.

ESTIMATED	<b>FERTILIZER</b>	REQUIREMENTS	FOR	1980	NUTRITIONAL
		DEVELOPING C			
	(Million tons	plant nutrient	N. P.	D. K.(	

	The second product matrices IV, FtOI, K	<b>U</b> )	
--	---	------------	--

	1939/60	1980
Asia and the Far East	2.53	20.0 •
Near East	0.25	3.6
Africa	0.40	8.6
Latin America	0.82	7.3
Τσται		39.5
Adjustment for expansion in arable land		9.5
Net requirement		30.0

\* Including 5 million tons for China (mainland).



Bount : P. W. Parlay, " Paralliano and Bonnessie Devisionant" super delivered at the Perillian Workshop, American Bactor of Soil Solence Parden University, Petersny 13-13, 1960.

pue IV.1. Average relationship between finitizer use and value index of orap production (per arable bestare, 42 countries, 1906-50) and utilizing the average relationship between average crop yield and fertilizers use given in figure IV.1. Moderate rates of growth in fertilizers consumption were assumed for countries that have already attained a high use of fertilizers. Using 1960 as a base, the assumed targets for food supply ranged between 174 and 219 per cent.<sup>31</sup> Rough adjustments were then made to take into account the increase in food supply that might be attributed to a possible increase in arable land.

102. It should be emphasized that these estimates are not projections of effective demand for fertilizers. It is unlikely that these targets would be reached without much greater efforts than have been made in the past for promoting the use of fertilizers in developing countries. They are estimates of requirements that may be needed to attain defined nutritional goals under given assumptions. These goals assume, *inter alia*, a sustained rate of growth in agricultural output ranging between a rate of about 3 per cent for Africa and 5 per cent for Asia and Far East. To emphasize the magnitude of such a task, one may refer to the fact that a sustained 5 per cent growth in agricultural output has not been attained in the past by any of the world regions; and only a few countries have succeeded in attaining such high goals for a period extending over ten years. These production goals compare favourably with those incorporated in the development plans of various developing countries.<sup>30</sup>

103. On the basis of the total fertilizers requirement given earlier, the amount of nitrogenous fertilizers required may be estimated to increase from 9 million tons in 1961/62 to 25 million tons in 1980. These figures were computed by using the ratio of nitrogenous fertilizers to total 'ertilizers given in table IV.7.

as Parker, op. cil.

#### NITROGENOUS FERTILIZER REQUIREMENTS, 1980 (Millions of tons N)

															1961	/900
Asia and Far E	ası .														t.63	
INCOLF ICASL															.34	8.0 2.0
AID CAL															.t4	t.9
Latin America.	• •	·	•	•	·	·	·	•	·	·	·	•	•	·	.46	t.9
															2.57	t3.8
Advanced coun	l ries	•	•	•	•	·	·	•	•	•	•	•	•	•	6.58	t0.5
								G	R/	N	D ·	<b>T</b> 0	TA	L	9.15 •	24.3

· Excluding centrally planned countries.

 <sup>&</sup>lt;sup>81</sup> Set largets for 1980 (1960 - 100):
 174

 Africa
 174

 Asia and Far East
 219

 Latin America
 194

 Near East
 194

## 2. MARKET RESEARCH - ESSENTIAL TO PETROCHEMICAL DEVELOPMENT

## F. O. Kaupp and R. F. Neu, Marketing and Supply Department, Esso Chemical Company, Inc., New York

Most of the plastics, synthetic fibres, elastomers, agricultural chemicals, detergents, resins and surface coatings consumed today are either wholly petrochemical in nature or partially based on petroleum-derived feedstocks. Most of these materials are produced in multimillion or thousand million pound quantities.

Probably more than 75 per cent of petrochemical production is accounted for by North America, Western Europe and Japan, which were heavily industrialized and populated nations even before 1939. Not surprisingly, these areas are the leading producers and consumers today. In other words, less than 25 per cent of the world's population is responsible for the production and consumption of more than 75 per cent of the major petrochemical products.

The development of the petrochemical industry in these countries followed more on less the same pattern. In the beginning, a few producers with technology, whether their own or acquired, who had faith in their ability to market the products and were willing to take a financial risk, entered the market. Pent-up consumer demand as a result of the Second World War and the novel uses of the final products led other companies to develop or acquire similar process technology.

The end result was that as supply caught up with demand, producers looked at each others' products as a means of attaining still greater sales volume. This resulted in rapid expansion and the installation of plants of large capacity producing almost identical products. Although larger plants are capable of lowering unit costs, they must operate at high rates of capacity to remain economically efficient.

To attain and hold operations at a high level of efficiency, it was natural for the focus to shift from manufacturing to marketing. While it was relatively easy for technically oriented petroleum and chemical companies to pin-point expenditures for plant, equipment, research, engineering, etc., there seemed to be a lack of knowledge regarding the best way to obtain a share of the market. Dr. Theodore Levitt,<sup>1</sup> a lecturer on business administration at Harvard Business School, states the following: "There are three pre-eminent facts of modern economic life that every company has to know and reckou with:

"(1) The accelerating rate of change;

"(2) The growing similarity of competing products; and

"(3) The growing sophistication of the customer."

The difficulty that many of these companies faced was that of measuring the customer's needs, and of ascertaining who he was and what kinds of products he would purchase. Usually a mistake made in estimating the cost of construction of any chemical plant is not nearly as serious as over-estimating the market and/or unit price that the market will support. The growing complexity of the market-place led to the development of new techniques which, for lack of a better name, are usually referred to as market research.

Market research staffs are usually charged with the responsibility of examining and projecting markets, most often for a period of two to five years, which corresponds with the time it takes for a new plant to be constructed and operating. Some of the most important elements of Market Research are summarized in the table<sup>s</sup> below:

#### ELEMENTS OF MARKET RESEARCH

- 1. The size of the total market past, present and future.
- 2. The production of the chemical locally and the capacity of the manufacturing plants, present and future.
- 3. The volume of exports from and imports into the local market, with forevasts of future trends.
- The competitive position --- who the manufacturers and suppliers are. What alternative products can compete. The extent of the captive market.
- The present and likely future share which one's company can expect.
- 6. Current price levels and future price trends.
- Influence of duties, tariffs and quotes, and also the significance of trading communities like EPTA, the EEC (or ALALC).
- 8. Special market requirements necessary to ensure the future success of the marketing operation.

<sup>&</sup>lt;sup>1</sup> Dr. Theodore Levitt, Harvard Business School, Talk before chemical machaning and economics group, A.M.C.S., Chicago, Illinois, 6 Suptember, 1961.

<sup>&</sup>lt;sup>4</sup> Presented by H. P. Hedge, Easo Petroleum Company, Ltd., at ASLIB Chemical Group, London, 4 April 1963.

Although market research is costly in time and manpower, the fact that it is a worth-while exercise when committing millions of dollars to the construction of a new chemical project has been shown by J. Lloyd Johnson, Manager of Plastics Marketing Research, Dow Chemical Company:

"Data on production cost and capital are now as pecurately derived as seems feasible, and appraisal methods exist that can accurately reflect every possible foreseen profit-affecting situation. The challenge now is for sophisticated and accurate market appraisals.""

The following table shows the importance of accurately predicting unit sales price, raw material yield, unit sales volume and fixed capital requirements. The case presented assumes a 10 per cent mis-estimate in each of these factors and shows the relative error created in the DCF (discounted cash flow) return. The example is based on a hypothetical acrylonitrile venture.<sup>4</sup>

PER CENT ERROR INDUCED IN TOTAL APPRAISAL OF HYPOTHETICAL ACRYLONITRILE PROJECT BY A 10 PER CENT MIS-ESTIMATE

In sales price	In raw material yield	Unit sales volume	Fixed capital
38	28	t5	8

The question of accurately projecting sales price is shown to be extremely important.

The effect of cutting prices can also seriously affect profit margins. For example, if sales were based on a 10 per cent margin and it is found necessary to reduce the unit sales price by as little as 4 per cent, it is necessary to increase unit sales by almost 67 per cent merely to maintain the mane economic efficiency (assuming the plant is operating near capacity).

In other words, a 4 per cent decrease in price requires selling 2/3 more merchandise than had to be sold at the regular price. The problem frequently is whether or not it is likely that a 4 per cent price cut will really boost sales by 2/3. Most markets are not sufficiently elastic for a price cut of this magnitude to increase the market enough to maintain profits.

Frequently, in order to fill up a plant producing at something less than capacity, the manufacturer feels he can rely on exports. At a talk before the Société Chimie Industrielle, Mr. R. M. Jackson of Esso Chemical Company stated:

"The large highly developed countries are in an excellent position to export. Smaller countries will seek export markets in order to make local manufacture

more attractive but will find it difficult to compete with the first group. Small countries will no doubt install capacity for local production if their markets are at all sizable, even though these markets need to be protected by duties. Countries which will not be able to justify local plants will have relatively small markets. Therefore, the total export market for any given product will tend to become quite small, yet many countries will have the ambition to follow these small markets.

"However, with the interest of so many groups participating in petrochemicals, it is bound to become increasingly competitive and profits will accrue only to those who can carry out their activities based on sound business principles and mature judgement." <sup>5</sup>

Putting it another way, Mr. John G. Gillis, Vice President of Monsanto Chemical Company, stated:

"More important, competitive advantages never seem to last long enough to cash in on them. You have to run pretty fast just to stand still. Too often a market survey for a new product is just that and no more. If it tells me only the size of a given market and estimates its growth potential, this is only a fraction of the total picture I need to make a decision. What I really need to know, is my market 'fit'? How do I reach the market and at what cost? Does reaching it draw on my present sales strength or require new ways? What is the nature of my competition - its strength and weaknesses? What is the outlet for raw materials prices and accessibility? In short, I need answers which will evaluate the marketing risk of the total project. I am not holding market researchers responsible for technical evaluation, but too often marketing research stops short of the total marketing problem." 4

It appears then, that there is general agreement on the need for market research. However, it should not be presupposed that performing market research obviates the need for research, development, engineering, manufacturing, design, product application, quality control and customer servicing. The following case histories illustrate some of the approaches to chemical market research and some problems which can arise.

Although our company has generally found that people with training in chemistry or chemical engineering can make good market researchers, we realize that many companies prefer to use economists who, for the most part, lack a technical background. A few years ago we had an experience with a large country studying its rubber requirements. Their economists' analysis found that during the next ten years, indigenous natural rubber production would be unable to meet its needs.

As a result, they decided that polybutadiene and polyisoprene synthetic rubber plants should be built since these "were the newest materials in research in the

<sup>&</sup>lt;sup>8</sup> J. Lloyd Johnson, "Your New Project, How Profitable?" Chemical Week (21 July 1960).

<sup>&</sup>lt;sup>4</sup> Assumption for acrylonitrile plant based on yield and fixed capital data from *Industrial Chemicals*, by Faith, Keyes and Clark, 1957. Production volume 40 million pounds/year with fixed costs at 5.2 cents/pound and variable costs 13 cents/pound. Depreciation on declining balance basis at 7 per cent per annum. Corporate income tax rate at 52 per cent. Process used is acetylene-hydrogen cyanide starting from anomonia, methane and acetylene.

<sup>&</sup>lt;sup>6</sup> R. M. Jackson, "International Trends in Chemical Business", Meeting of the Société Chimie Industrielle, Chateau de Menars, France (April 1967).

<sup>&</sup>lt;sup>4</sup> J. G. Gillis, address before the Chemical Marketing Research Association, Pocono Manor, Penn., 24 September 1962.

United States". We were asked of our interest, together with several other companies, in building the stereorubber plants they proposed or in supplying the necessary raw materials. During the course of the next several months, we spent several man-years of total effort in re-examining not only the rubber industry, but also the entire chemical complex in the country to understand the intra-relationships. Our own study showed that:

- 1. Maximum use was not being made of the areas suitable for producing natural rubber. Fertilization and replanting with selected clones would have been more economic and preferable to spending their limited foreign exchange on synthetic plants or rubber imports and would, at the same time, build up local production of natural rubber. In addition, several of their bilateral trade agreements with other countries were based on receiving natural rubber imports as payment for their export of other goods.
- 2. The economists proposed using formentation alcohol to produce the butadiene (raw material for the synthetic rubber). Except under special conditions, this is an obsolete process. Also, our projections for other local chemical markets, which could be logically based on ethanol, showed that the fermentation industry would not be able to supply total needs if butadiene as well as the other materials were manufactured.
- 3. At that time, the special uses for the stereorubbers suggested they would be particularly useful in high speed tyre applications. However, road conditions within the country precluded fast driving.

As a result of our studies (and for additional reasons), we decided not to participate in this venture. Eventually, a styrene-butadiene rubber plant, dependent on alcohol feedstock, was built. The plant, operating today, provides limited grades of product at considerably higher prices than those prevailing in the rest of the world.

At the risk of generalizing on the basis of this specific example, we feel there are several points to be made:

- 1. Efficient use of existing domestic industries based on natural resources is preferable to the outlay of needed foreign exchange and technical skills.
- 2. The availability of know-how and technology for proven products (in this case, styrene-butadiene rubber) are usually greater and more reliable than for new products that still have to stand the test of time.
- 3. The products chosen should fit the conditions and needs of the country. Because the United States manufactures a particular product, it is not axiomatic that it would be the *best* product to manufacture somewhere else.
- 4. If obsolete processes or chemistry are used, or if production volume will be small by world standards, with unrealistic and high prices required to sustain the investment, a careful analysis should be made to determine whether this constitutes the kind of "progress" the country truly desires. Perhaps such investment monies could be better spent in industries where the country would be fully competitive with

the rest of the world, or, preferably, in industries where they would possess an advantage. Under present world conditions, large size plants are required to be fully competitive in raw material production. This suggests that an easier road to travel might be by investment in secondary or even tertiary industries fed temporarily by imported raw materials. Hong Kong's success in the world market for plastic flowers is an interesting example of a successful industry using imported raw materials to create finished goods exports which are fully competitive in all world markets.

Another example of the need to mesh technology and market research, centres on the plan of a major chemical company to produce trimethylol-propane for polyurethane processing. Although this had been the material used in early polyurethane synthesis development work in Germany, a little chemistry showed that any polyhydric alcohol or ether having terminal hydroxyl groups would also be quite suitable.

Unfortunately, the chemical suitability of using alternative materials, such as low-cost polypropylene glycol, which had been available in the market place for many years, was overlooked. Such glycols were functionally proper but not considered and a large plant was subsequently built for trimethylolpropane. Fortunately, other uses were developed for trimethylolpropane as time went on, but when the plant came on stream, the market outlook was indeed grim. Obviously, then, one of the things we should train our market researchers to do is to deal with the entire problem and not just one facet of it.

The critical evaluation of competitors' potentials (or a neighbouring country's plans) should also help shape investment strategies. Failure to examine adequately or to make maximum use of commercial intelligence efforts are more than amply illustrated by the market situations which have developed in many chemical products, such as linear polyethylene, benzene, orthoxylene and perhaps, phthalic anhydride. In the pursuit of an attractive contract, the need to consider the nature of the other possible competitors for the same business and the relative strengths and weaknesses of each, should not be forgotten. Wise market research safeguards raw material investment by analyzing the customer's likely outlets for the products manufactured from those raw materials.

Not very long ago, a chemical company asked us to supply large quantities of an olefin used in the synthesis of a plasticizer component. Because of the large volume desired, we would have had to supply their requirements from several manufacturing locations. Also, there was the probability that additional investment would have to be committed to manufacture still more of this material.

We analysed our customer's markets because of both these factors. As a result of our study, we found that our customer was either on the verge of a major breakthrough or had grossly over-estimated the established markets into which it could move. This study also carried us into examining their chances of exporting the material to other trading areas. Such areas, however, had nowhere near the consumption of products utilizing this material to match the market outlet we were seeking.

We therefore concluded that it would be quite risky to commit additional investment and that their requirements could probably be satisfied from our existing supply points.

History proved our market research was correct. We later learned they had not made any study, but had based their estimates on assuming that past percentage growth rates would be maintained over the coming five-year period.

Most market research studies include a presentation of statistical information to quantify market conditions. Expected and past production, sales, consumption, and exports or imports are usually documented. Rarely, however, are official sources of data available or reliable. Frequently, Government statistics lump several products, not always related, into one number or "basket category".

Only in unusual cases is the market researcher able to check the export figure from one country with the import figure reported by the receiving country. It would appear that all countries could do a better job of providing meaningful statistics. Industry should be more than willing to contribute opinions, recommendations and ideas concerning coverage and reporting systems.

Regardless of the source of data, it is possible to distort trends and even develop misleading forecasts by choosing to present the plot on arithmetic rather than logarithmic co-ordinates.

Mr. Leonard H. Lempert, Director of Statistical Indicator Associates, has commented as follows about the use of arithmetic scales.

"Management constantly thinks in terms of growth rates and percentage comparisons, which automatically presupposes the use of logarithmic scale charts. Yet, attempts by market researchers and statisticians to introduce logarithmic charts have consistently been met with almost fanatical management resistance to the use of complicated devices."

"Logarithmic charts tell an important story. Comparison of slopes immediately shows whether the company sales, for example, have risen or declined at lesser or greater percentage during two periods under comparison (the steeper the slope, the greater the rate of change).

"The graphs presented in the attached figure I show what happens if annual production of formaldehyde is compared with the annual Federal Reserve Board index (FRB) for organic chemicals on arithmetic and logarithmic plots.

"The arithmetic charts suggest that formaldehyde output is growing at a much faster rate than organic chemicals production as a whole. The figure shows that arithmetic charts give greater weight to absolute change than to relative changes.

"It is obvious that the two curves on the logarithmic chart are virtually parallel -- which means that the

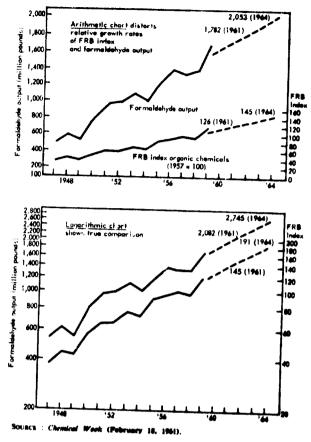


Figure I. Arithmetic vs. logarithmic projections

percentage rate of growth is essentially the same in both series and that formaldehyde output is not, over the long range, growing faster than output of organic chemicals as a whole."

Statistical records of consumption are useful in that they show us where we have been. There is a matural desire to extrapolate this information to tell us something about the future. L. S. Mumford of Imperial Chemical Industries, Ltd., describes<sup>a</sup> the experiences of Professor Edwards, Chairman of the Electricity Council, and Mr. Clark of the Central Electric Generating Board, who wrote a paper in 1962 entitled "Planning for Expansion in Electric Supply". In their paper they had shown the growth of power demand in England and Wales from 1920 to 1961. Edwards and Clark sought the aid of modern computing facilities and worked out some eleven mathematical expansions, all of which fitted the data that had been covered over the past forty years.

However, when these equations were used for extrapolation, they gave very different results even over the next ten years. As they say, "here we have to mart

<sup>\*</sup> Loonard H. Lomport, "Paril in Numbers", Chemical West (18 Pobrany 1961).

<sup>&</sup>lt;sup>6</sup> L. S. Munford, "The Longlines of the Long Range Porecesser", Chemistry and Industry (9 November 1965).

applying judgement". The authors concluded that it was best to stick to the simplest exponential curve as "there appears to be no convincing reasons for preferring a more complicated formula". There is a danger that the computer may cause confusion, helpful though it is, to the long-range forecaster.

A frequently used statistical device is the Gompertz curve. To use such curves effectively, it is usually necessary to have good statistical information over a long period of years. Most of the developing countries in many cases do not have such long histories themselves and to project such curves on the basis of the meager information available can be very risky.

In the following table, we have shown the results of using Peter W. Sherwood's Gompertz curve extrapolations to predict polyethylene consumption for the years 1960 and 1961.<sup>9</sup>

## POLYETHYLENE GOMPERTZ FORECAST

#### (Thousand million pounds)

Data basis	1944-1952	19 <b>44-1936</b>	1944-1959	Actual
Forecast for:				
1960	8.3	7.5	6.6	6.1
<b>1961</b>	9.1	8.4	7.3	6.6

As expected, the spread between extrapolation and actual performance narrows as the forecast becomes shorter-range. Note also that in this case, the data base is not extensive but the market was already in the initial growth stage characterized by a rapid upward movement and Gompertz's extrapolations actually were quite good. In the case of major segments of the economy, this trend may be quite significant and the forecast quite often approaches the actual realization quite closely. While the advantage of using the Gompertz forecast may be that it is possible to calculate the future without spending time on field calls, it is doubtful if this approach would be suitable in newly developing economies. In developing economies, rapid strides are made in short time spans and reliance on purely statistical devices would more than likely not realistically predict the future five or eight years.

If we had relied upon purely graphical representations of the market for fertilizers in many of the countries in which we have decided to build plants during the past three years, we would have concluded that there was little possibility for success. We have found, instead, that it is more realistic to gather as much information as possible from personal interviews and by contacting industry leaders, government institutions, universities and consumers, before making the forecast.

After the forecast has been made, plotting the data can serve as a useful cross check to see if the discontinuities in the future in anticipated demand are logical. This does not mean that statistical curves and representations are not useful tools, but we prefer to use them as a checking device rather than as the basis of our projections.

While chemical markets will probably always be influenced by human judgement, "hunches", and promoters, market research has demonstrated a good enough record of success to suggest that an investment made without it invites unnecessary risks. It also suggests that it is necessary to keep constantly in touch with the people in the industry because of the rapidity of product obsolescence, new competitive activities, and new product applications.

Considering that many of the developing nations are located in the same geographical area, it would also appear that the experience of the United States of America the Latin American Free Trade Association (ALALC) and the European Economic Community (EEC) should be given careful consideration in planning area rather than country development programmes. Albeit, this would require Governments to remove some of the present duty and tariff barriers in force against their neighbours. Elimination of trade barriers could encourage the development of diverse industries which could draw upon the combined area market. The exchange of products on an equal value basis between nations would encourage investments which could not be made if the plant had to depend on the local market alone.

The developing nation may also wish objectively to assess its attractiveness as an investment area. Most of the major technically oriented companies are constantly seeking new investment opportunities. Together with their investment dollars, they bring a wealth of technology, manufacturing and marketing efficiency, new construction techniques, and product know-how not available from other sources.

Emilio G. Collado, Director of Standard Oil Company (New Jersey), in an address at Lehigh University, made the following remark concerning the importance of recognizing the problems of the developing nations:

"The central economic problem of our time may turn out to be the task of devising an effective collaboration with the less developed regions of the world. This is not primarily a matter of humanitarian concern, although this concern is far from absent. It is not because our economy will benefit from having more prosperous trading partners, although this also is true. It is not for fear that the rich may be getting comparatively richer, for even if it could be shown that the rich were getting richer matively, it may certainly be shown the poorer are getting less poor in absolute terms. It is in fact, not because vast areas of the world are undeveloped, but rather because they are developing."<sup>10</sup>

We have attempted to present a brief exposition of market research techniques and problems. We hope we have not over-emphasized the things that are to be avoided in performing market research. However, the

<sup>\*</sup> Peter W. Sharwood, "Use This Correlation For Poresesting Petroshamical Markets", *The Nydrocarban Processing and Petroloum* Aginer, 43(1), January 1963.

<sup>&</sup>lt;sup>10</sup> Emilie G. Collado, " Beonomic Development and the Search for Stability", statement made at the Symposium on the Problems of Peace and War, Lehigh University, 25 October 1963.

advantages of having pertinent and realistic information available summarizing the strength, size and importance of the nation's industries, where they are located, and their hopes and plans for the future, would provide the impetus for further development.

The importance and extent of transportation and communications facilities, location and accessibility of markets, raw materials availability, retail outlets, disposable income, and an estimate of the economically effective "purchasing public" should be part of the economic inventory of any nation. Whether or not the information is to be used by public or private enterprise, it should provide the foundation for viable investments. The determination of who the customers are and what their

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requirements are is an essential part of the over-all market appraisal.

If chemistry, engineering, and marketing know-how are to be combined to achieve industrialization, we believe that the application of sound market research principles is mandatory. Properly applied, these techniques should materially benefit certain sectors of the growing economy, especially those concerned with food, clothing, and shelter. The combined talents of industrialists, educators, and governments working together to selve the problems not only of manufacture but also of distribution, shipping, and communications, appear to be needed urgently to solve the problems of underfield, underelisthed, and underhoused populations.

ಯು ಸಂಗಾರ ಸಂಗ್ರೆ ಕೇಳಿದ್ದರೆ. ಇದು ಸಂಗ್ರಹಿತ್ಯಾಗಿಕೆ ಸಂ ನಿಂದಿ ದೇವಿ ಆಗ್ರಹಿಸಿಕ್ಕೆ ಭೇಗಿಯಾಗಿ ನಿಂದಿ ಮಾಡಿಕೊಡ್ಡಿದ್ದಾರೆ. ಕೇಳಿಕೆ ನಿಂದಿ ನಿಡಿದ ವರ್ಷಗಳ ಮಂಡಿದ್ದರೆ.

## 3. THE ROLE OF THE DOMESTIC MARKET IN THE DEVELOPMENT OF PETROCHEMICAL INDUSTRIES AND THE NEED FOR EXPORTS IN RELATION TO ECONOMIES OF SCALE

United Nations Centre for Industrial Development

#### INTRODUCTION

In their drive towards economic development, developing countries have been attaching special importance to the role of the industrial sector. The "classical" and predominant pattern for the development of this sector in these countries has been primarily to concentrate on import substitution industries. Such a policy is likely to result, in the long run, in the development, under the umbrells of heavy protection, of high-cost industries. This is particularly so in the case of industries characterized by significant economies of scale for which the local market is too small to permit exploitation. Within the framework of this pattern of industrial development, the export-oriented industries are concentrated in the field of light industries and labour-intensive industries such as textiles, and, by and large, these industries have been characterized by stagnant demand.

An alternative to the above pattern of development has been elaborated in a paper presented by the United Nations Centre for Industrial Development to the United Nations Conference on Trade and Development.<sup>1</sup> It is suggested that in the long run developing countries may attain a faster industrial growth and hence economic development by concentrating on the development of certain dynamic industries; these, in contrast to the industries with stagnant demand, are characterized on the supply side by high capital intensity. Such a pattern of development would involve, inter alia, a greater capital supply than has so far been flowing into the industrial sector in developing countries, the development of a more sophisticated industrial and economic structure, and a longer maturation period for investment, and in the short run these factors may have adverse effects on the balance of payments.

The intention of this paper is to present for discussion several important implications and possible alternative approaches and suggested solutions for the development of petrochemicals for export. Its scope precludes a detailed treatment and analysis, particularly with respect to identifying the various petrochemical operations having export potential. This would require more detailed studies

relating to a country or region and taking into consideration a number of factors, including inter alia wider coverage of petrochemical operations, and the interaction of economies of scale, alternative technologies, transport cost and new development in transport techniques. Chapter I presents some important economic characteristics of this industry, including economies of scale and cost structure, and examines briefly the possible effects of the transfer of technology from developed to developing countries. Chapter II indicates the comparative growth of the petrochemical industry, and consumption pattern and trends for plastics, synthetic fibres, synthetic rubber and nitrogenous fertilizers. Chapter III examines the various implications for new entrants from developing countries into the international market. These last two chapters rely heavily on data obtained in a United Nations paper presented to this Conference on trends in production, consumption, and trade for selected petrochemical products.\*

#### I. ECONOMIES OF SCALE AND COST STRUCTURES IN PETROCHEMICALS

A well-known and important economic characteristic of the petrochemical industry is that of returns to scale. These are attributed to a number of factors. In the first place, total fixed investment increases less than proportionately to plant capactity, owing to the fact that doubling the \_ pacity of unit equipment would require less than double the amount of steel, labour and overhead cost, thus resulting in a reduction in the average cost of producing larger units of equipment. Erection cost behaves in a similar way. Further, a large capacity plant may, in comparison to a smaller plant require only a small expansion in auxiliary facilities such as laboratories, workshop and offices.

Furthermore, great economies of scale also obtain in labour requirements; the number of operators varies only slightly with an expansion in the plant capacity and labour in auxiliary activities such as maintenance labour increases less than proportionately to capacity. Similar relationships are known to exist with respect to overhead cost.

<sup>1 &</sup>quot;General study of experts of manufactures and sami-manufactures from developing countries and their rate in development", paper propared by the United Nations Centre for Industrial Development, for the United Nations Conference on Trade and Development, 18 Petersny 1966 (B/CONF-46/11).

<sup>&</sup>quot;Recent trends in production, communition, trade and endness in adjusted putrochamical products", paper proposed by the United Matiens Cantro for Industrial Development for advant

 TABLE 1. VARIATIONS IN AVERAGE PRODUCTION COST FOR SELECTED PETROCHEMICAL OPERATIONS, SMALL VS. LARGE CAPACITY PLANTS \*

 (Unit co-efficient assigned to largest capacity)

Petrochumical operation	Capacity factor											
	1	2	j	4	3	6	7		9	10		
Ammonia (ex. natural gas)	1.50		1.20		1.06							
Michanoi (ex. natural gas)	1.47				1.00	• •	1.6	-	-			
Acetylene (ex. cthane)		••		1,12	• •	••	1.04	• •		1.00		
Fihylene (av. ethane)	1.62	• •	1.17	••	1.00							
Ethylene (ax. ethane)	2.00			1.40				1.00				
Urea.	1.90		1.35		1.00	••	••	1.00				
simmonium nitrate	1.46	1.19	1.12	1.00						-		
Acrylonitrile (ex. acetylene and hydrogen cyanide)	1.47			1.00		-		-				
inyl chloride (ex. acetylenc and hydrogen chlo-	1.4/	1.13	1.00					_	-			
ride	1.66	••		1.19		• •	••	1.00	_	_		

Souaca: Calculations based on data obtained from the following publications, these data being made comparable so far as possible: W. Isard et al., Industrial Complex Analysis and Regional Development, (London, Chapman and Hall, Limited, 1959) and "Utilization of Natural Gas in Petrochemical and other industries"; paper prepared by the United Nations Centre for Industrial Development and presented al the Second Symposium on the Development of Petroleum Resources of Asia and the Far East, Teheran, 1-15 September 1962.

• Small and large-scale capacities were assumed as follows (in thousand ions of annual capacity):

			•															<b>CHANNE</b>	LATEL
Ammonia .																		30	200
Methanol								-					•	•		•	•		
Methanol .	•	•	•	•	•	•	•	٠	٠	٠	•		•	•		•		- 30	300
AVELY ICINE .																		12.5	63
CULY OF																			
Dimin				•	•		•	•		•		•	•	•	٠	٠	•	30	240
Ures	1		1	•	•	٠	•	•	٠	•	•							20	100
				Ε.														50	200
Vinvi Chlor	i	. '	•	•	•	•	•	•	•	•	•	٠		•	•		•	20	60
Vinyi Chlor		ι.	٠	•	•	٠	٠	٠	٠	٠	•	•	•	•				12.5	100

Economies of scale in production cost are illustrated in table 1 for a number of petrochemical products,<sup>8</sup> indicating an increase in average unit cost in a smallscale operation ranging between 40 and 100 per cent as compared to large-scale operations, the production cost of which was assumed to equal 100. The rate of increase in average unit cost is highest in small capacity plants and gradually decreases in the larger capacity plants.

For the same petrochemical operations, the distribution of the various cost components in production cost is illustrated in table 2. With respect to urea, ammonium nitrate, acrylonitrile and vinyl chloride, the composite cost of production was calculated to introduce the capital, natural gas, petroleum, and other inputs carried over from petrochemical product used as raw material in the respective operations, i.e., ammonia, acetylene, methanol etc. These cost estimates do not reflect the actual performance of any particular plant and are based on engineering and economic coefficients taken from the United States experience. They may however be used to illustrate the order of magnitude for the share of the major components in production cost.

The distribution of production cost indicates the predominant share of capital charges, which include depreciation and interest, and the rather low share of labour. It also indicates the great decrease in the share of labour cost with the increase in plant capacity. The share of petroleum and natural gas as raw material and fuel is important for basic intermediates and decreases at the subsequent stages of petrochemical operations. Further, the share of this component of cost increases with the size of plant capacity. The cost of maintenance, supervision and general plant is an important share of the total cost. With respect to utilities including electric power, fuel and water, their shares vary with petrochemical operations and processes, between 2 and 20 per cent for the selected operations given in this paper.

Another important characteristic of the petrochemical industry is the predominance of industrial complexes, offering economic advantages that are derived from the close proximity of a number of related petrochemical operations. Capital requirements are reduced when a number of operations are placed in close proximity, mainly because of the use of common auxiliary facilities and a reduction in installation and erection costs. For example, when comparing the cost of hypothetical large and small complexes of nitrogen fertilizers with that of erecting separate individual plants,4 it was estimated that fixed plant investment might be reduced by between 20 and 30 per cent. Furthermore, reduction in production cost may be attained also by the sharing of labour in auxiliary facilities, the reduction in overhead cost, the reduction of transportation cost for raw materials and products etc.

In the past research has played an important role in the development of the petrochemical industry and this is expected to continue into the future.<sup>5</sup> This has involved both basic and applied research and covered the field of development of new petrochemical processes and improvement of the old, discoveries of new products and the development of new applications and improvement of the old. This required additional capital and cost, which have been borne largely by the industry.

<sup>\*</sup> Several documents presented to the Conference illustrate the return to scale in other petrochemical operations.

<sup>&</sup>lt;sup>4</sup> Studies in Economics of Industry (United Nations publication, Sales No.: 63 II. B.3).

<sup>&</sup>lt;sup>8</sup> See in this connexion "Recent trends in petrochemical research and development", Conference paper by Flaroid Hart.

TOTAL PRODUCTION COST COMPONENT IN TOTAL PRODUCTION COST, SELECTED PETROCHEMICAL OP	ERATIONS
(Percentage of total)	

Type of Operation (Small and Large)	Capital charges	Natural par petroleum	Urilities	Operating Jabour	Supervision and plans general	Maintenance	Others	Toial
Ammonia								-
Small	42.7 44.3	17.9 • 25.7	3.7 5.3	10.3 1.6	8.4	9.4	7.6	1 <b>00</b> .0
Methanol			<b>J</b> .J	1.0	2.6	9.9	10.7	1 <b>00</b> .0
Small         . <td><b>48.8</b> 52.9</td> <td>12.7 19.5</td> <td>1.8 2.8</td> <td>9.3 1.5</td> <td>7.5 1.2</td> <td>10.7 11.6</td> <td>9.2 10.5</td> <td>1<b>00</b>.0 1<b>00</b>.0</td>	<b>48.8</b> 52.9	12.7 19.5	1.8 2.8	9.3 1.5	7.5 1.2	10.7 11.6	9.2 10.5	1 <b>00</b> .0 1 <b>00</b> .0
Small.	36.3 30.4	12.9 20.6	13.0 20.7	7.8 3.9	11.1 7.4	11.9 10.0	6.9 7.1	100.0 100.0
Ethylene							7.1	100.0
Smail	<b>40.0</b> 32.3	17.2 29.6	8.5 14.6	5.5 1.5	10.0 8.0	11.3	5.7	100.0
Ures >				1.5	e.U	9.3	4.8	100.0
Small	44.9 46.2	6.1 * 13.0	<b>6.4</b> 11.2	11.1 4.4	13.3 6.3	11.3 11.2	7.0 7.7	1 <b>00</b> .0
Ammonium nitrate •					0.5	11.4	1.1	1 <b>00.</b> 0
Small	<b>40.7</b> <b>39</b> .1	<b>6.8</b> • 1 <b>2.</b> 3	13.7 19.3	9. <b>8</b> 4.2	11.2 7.6	10.1 9.4	7.5 8.1	1 <b>00</b> .0
Acr ylanierile »				•••		7.4	ð. I	100.0
Small	32.2 30.6	12.9 14.9	21.0 26.5	8.1 5.2	10.6 8.4	10.6 10.1	4.6	100.0
'myl chloride					0.4	10.1	4.3	100.0
Small	<b>31</b> .1 <b>26</b> .0	4.2 4.5	7.5 9.1	5.3 2.3	8.5 5.6	10.2 8.5	33.2 ° 43.9 °	100.0 100.0

Sounce: W. Isard et al., Industrial Complex Analysis and Regional Development (London, Chapman and Hall, Limited, 1959) and "Utilim-tion of Natural Gas in Petrochemical and other Industries "; paper prepared by the United Nations Centre for Industrial Development and presented at the Second Symposium on Development of Petrolsum Resources of Asia and the Far East, Teheran, 1-15 September 1962.

TABLE 2. DETERMINION OF MAR

· includes natural gas used as fuel.

· Composite cost was calculated to introduce the capital, natural sas and other inputs carried over from previous petrochemical stages.

· Includes hydrogen chloride.

The differential in the major cost components associated with locating the petrochemical industry in developing countries may now be briefly mentioned." These would of course vary from one location, country and production process to another, and an accurate assessment would require detailed study, taking into consideration, inter alia, the above factors; however, general observations may still be made in this respuct. Capital charges are expected to be higher in developing than in developed countries because of higher interest rates and the high investment cost, which is due to added ocean freigt t and insurance on imported equipment and materials, import profit and a possible difference in erection cost. Aside from direct investment in the plant proper, in developing countries, additional investment may have to be incurred in economic and social infrastructures, such as housing

and other social amenities for the labour force, transportation, power generating and water supply facilities."

As regards the use of petroleum and natural gas as raw material and fuel, their cost is comparatively low in oil-producing countries and therefore they tend to pull production cost down. As indicated in table 2, this would affect the production cost significantly in the production of basic intermediate chemicals but only 'o a much lesser extent in subsequent petrochemical operations. This gives these countries a possible comparative advantage in the production of the former petrochemical operation.

With respect to maintenance, the relatively low wages in developing countries tend to reduce cost. However,

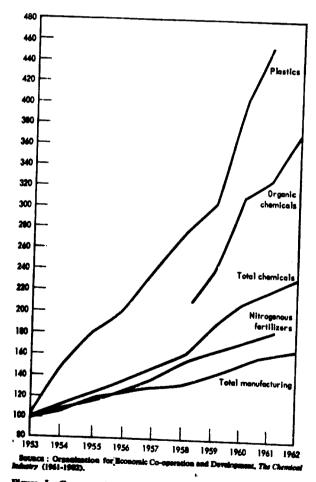
<sup>·</sup> fan St din la . t of Juliutry (United Natio ille pr ica, Sales No.: 63.II. B.J.

<sup>&</sup>lt;sup>7</sup> Buch investment, however, may be treated independently of rect investment since it affects production cost through other sizes of production, i.e., cast of inbour, power, transportation, IT 010.

RATES OF GROWTH OF CONSUMPTION FOR SELECTED PETROCHEMICAL PRODUCTS AND OTHER INDICATORS, WESTERN EUROPE AND UNITED STATES OF AMERICA \*

(ber cent per annum 1930-1962)         Total manufacturing.       5       5         Total chemicals       9       6         Petrochemicals       9       6         Plastics.       17       9         Synthetic fibres.       28       16         Synthetic rubber.       26       7         Nitrogenous fertilizers       7       8         Others       6       3         Aluminium       8       4         Steel       6       (0.4)		Western Europe	United States of America
Total manufacturing.       5       5         Total chemicals       9       6         Petrochemicals       9       6         Piastics.       17       9         Synthetic fibres.       28       16         Synthetic rubber.       26       7         Nitrogenous fertilizers       7       8         Others       6       3         Steel.       6       (04)		(per cent per and	
Iotal chemicals       9       6         Petrochemicals       9       6         Plastics.       17       9         Synthetic fibres.       28       16         Synthetic rubber.       26       7         Nitrogenous fertilizers       7       8         Others       6       3         Aluminium       8       4         Steel.       6       (0.4)	Total manufacturing.	5	
Plastics.       17       9         Synthetic fibres.       28       16         Synthetic rubber.       26       7         Nitrogenous fertilizers       7       8         Others       6       3         Aluminium       8       4         Steel.       6       0	Total chemicals	-	•
Synthetic fibres.       28       16         Synthetic rubber.       26       7         Nitrogenous fertilizers       7       8         Others       6       3         Aluminium       8       4         Steel.       6       (0.4)	Petrochemicals		-
Synthetic fibres.       28       16         Synthetic rubber.       26       7         Nitrogenous fertilizers       7       8         Others       6       3         Aluminium       8       4         Steel.       6       (0.4)	Plastics.	17	A
Synthetic rubber.       26       7         Nitrogenous fertilizers       7       8         Others       7       8         Cemeni       8       4         Rubber       6       3         Aluminium       8       4         Steel       6       (0.4)	Synthetic fibres.		-
Nitrogenous fertilizers         7         8           Others         7         8         4           Cement         8         4           Rubber         6         3           Aluminium         8         4           Steel         6         (0.4)	Synthetic rubber.		
Others         8         4           Cement         8         4           Rubber         6         3           Aluminium         8         4           Steel         6         (0.4)	Nitrogenous fertilizers	20	•
Rubber         6         3           Aluminium         8         4           Steel         6         (0.4)		,	8
Rubber         6         3           Aluminium         8         4           Stoel         6         (0.4)	Cemeni	8	4
Aluminium	Rubber	6	7
Steel. 6 (0.4)	Aluminium .	8	3
Cotton (U.4)	Steel		
	Cotton.	1	

<sup>•</sup> Calculations based on value added in total manufacturing and chemicals. For the rest of the items, calculations are based on total consumption by weight.



Pigure I. Comparative growth of total manufacturing, chemicals and selected petrochemical products, western Europe (1953 – 100)

during the early years of operation, lack of training and lower factor performance may result in higher labour unit cost. In the longer run, if programmes of regular planned maintenance are organized and enforced, the wage cost of maintenance should actually be less than in developed countries once the skills have been acquired, because of the lower wage rates. An offsetting factor is the higher inventories of spare parts that must be carried to guard against an expensive shutdown; these are likely to be much higher in a developing country which is far from source of supply of equipment.

Differentials in the cost of utilities are expected to vary greatly with each country. Countries having access to a cheap fuel supply would obviously have a cost advantage; likewise countries endowed with hydro-power may have a cost advantage as regards power. On the other hand, in certain countries where auxiliary facilities such as power have to be supplied by the plants themselves, the cost of power and other utilities may be relatively high because of small operations and higher capital charges.

An important short-run factor associated with the transfer of technology is the possible low performance in production in developing countries as compared to production standards in advanced countries, which is attributed mainly to poor management and labour practices, resulting in an appreciable rise in unit production cost because fixed charges have to be allocated over a relatively small output.

#### II. TRENDS AND CONSUMPTION PATTERNS IN PETROCHEMICALS

Available data for western Europe and the United States of America indicate the comparatively high rate of growth of the petrochemical industry. Its dynamic growth may be illustrated by the faster growth in recent years of organic chemicals<sup>a</sup> as compared to total chemicals, and by total industrial production (see figures I and II). Similarly, for a number of petrochemical products, excluding nitrogenous fertilizers for western Europe, the annual rate of growth has also been relatively high, compared to the above-mentioned aggregate parameters and a number of selected products, textiles, cement, steel and aluminium.

This fast rate of growth is attributed primarily to high income elasticity of demand for a number of petrochemical products and to the gain through substitution from competing products; i.e., substitution in certain end-uses of plastics for lumber, metal and paper, etc.; synthetic rubber for natural rubber; synthetic fibres for natural fibres; detergent for soap, etc. The gain through substitution has been greatly enhanced by improvement in the properties and development of new applications for petrochemical products; introduction of new products with specialized properties and extensive promotion activities with respect to both industrial users and con-

<sup>&</sup>lt;sup>9</sup> It was reported in 1962 that 93 per cent of the basic material used in organic synthesis in the United States of America was obtained from oil or natural gas and for western Europe 63 per cent (Organization for Boonomic Co-operation and Development, The Chemical Industry, 1963-1963).

sumers. Furthermore, the prices for a number of these products have declined in absolute terms or in relation to competing products, giving further impetus to the substitution process.<sup>9</sup>

With respect to world patterns of consumption in petrochemicals, the major consuming centres are the United States of America, western Europe and other advanced countries. The share of various regions have changed since the beginning of 1950, as indicated in table 3, with the United States' share decreasing, while western Europe has become the major consuming centre for most of these products. The share of other countries has also increased; however, with the exception of nitrogenous fertilizers, it remains rather low. With respect to synthetic rubber the figures do not include the USSR, and scattered data available for this country indicate a probable consumption level similar to the total synthetic rubber consumption outside the United States of America.<sup>10</sup> On the other hand, the share of North America, western Europe and other advanced countries in the total consumption of nitrogenous fertilizers has declined, with the major gain recorded by centrally planned economies, from 11 per cent in 1955 to 18 per cent in 1963, and Asia excluding Japan, from 7 per cent to 9 per cent.

The potential demand for the years 1970 and 1975 was roughly estimated at two to three times the present

<sup>10</sup> See in this connexion: "Synthetics and their effects on agricultural trade", a paper presented by the Food and Agriculture Organization of the United Nations to the United Nations Conference on Trade and Development (E/CONF.46/39).

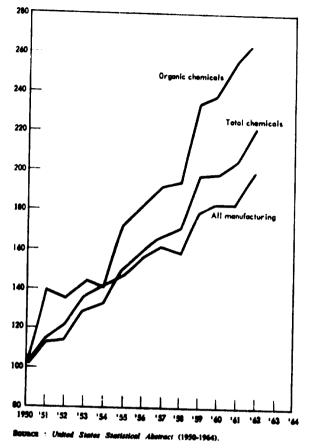


Figure 11. Comparative growth of total manufacturing and chemicals, United States of America (1950 = 100)

TABLE 3. SHARE IN CONSUMPTION OF MAJOR CUNSUMING CENTRES, SELECTED PETROCHEMICAL PRODUCTE	
(Percentage of total)	

	Western Bureps	North America	Other advanced countries *	Othere	Total
Plastics					••••••••
1950 · · · · · · · · · · · · · · · · · · ·	24.4 38.2	65.7 35.5	3.4 11.5	6.6 14.8	100.0 100.0
Synthesis fibres					
1930	12.1 41.1	78.2 29.6	5.3 16.0	4.4 13.3	100.0
huthoric rubber »				23.3	100.0
1950 · · · · · · · · · · · · · · · · · · ·	3.1 25.0	96.9 62.5	5.9	<u> </u>	100.0
Nacyonous forsilioors			••••	•••	100.0
1951/52	38.7 31.0	31.5 29.0	10.4	19.4 33.5	108.0 168.0

products ", paper propased by the United Postlens Contro for Industrial Destination of States

· Lines and included

<sup>&</sup>lt;sup>9</sup> See in this connextion: "Recent trends in production, consumption, trade and end-uses in selected petrochemical products", paper presented by the United Nations Centre for Industrial Development " above.

world consumption for four petrochemical products : plastics, synthetic rubber, synthetic fibres and nitrogenous fertilizers. These estimates indicate a slower rate of growth than those attained in the recent past.<sup>11</sup> They are made within a number of restrictive assumptions, and may be greatly upset by new technological development. The latter, it should be emphasized, has contributed greatly in the past to the growth of consumption, particularly with respect to plastics, synthetic fibres, and synthetic rubber, and is usually difficult to quantify and project.<sup>12</sup>

#### 111. IMPLICATIONS OF THE EXPORT MARKET FOR DEVELOPING COUNTRIES

Available data for the above-mentioned four categories of petrochemicals indicate a rather high share of trade in total production, ranging between 20 and 30 per cent. Moreover, the share of trade in total production for plastics, synthetic rubber and synthetic fibres recorded an increase over the last decade. These ratios become even higher, sharing about half the production, for a number of exporting countries and individual products within each of these four broad categories.

As table 4 indicates, western Europe is the major importing region while North America recorded a relatively small share of import, excluding nitrogenous fertilizers. On the other hand, Asia developed as an important market for nitrogenous fertilizers and along with Latin America has the next highest share in the import of these petrochemical products.

<sup>11</sup> Comparative annual rates of growth are as follows:

Plantin												19 <b>30</b> -1 <b>96</b> 0	1960-1975
Plastics	•											13	٩
												21	1
erauseik rubber												11	
Nitrogenous fertiliz	era	ı İ		•	•	•	•	•	·	•	•	11	8 10 9
<sup>18</sup> Op. cil.			•	•	•	•	·	·	•	·	·	8	4

Export again excluding nitrogenous fertilizers, is concentrated in a small number of countries; for plastics and synthetic fibres, the United States of America, the Federal Republic of Germany, the United Kingdom, Japan, Italy and France, and for synthetic rubber the United States of America and Canada.

As was indicated in chapter 1 of this paper, the importance of economies of scale in this industry cannot be over emphasized, especially in view of the small market of the developing countries for a number of petrochemical products. One approach to the efficient development of this industry may be through the pooling of regional or subregional demands. This would make it possible to take advantage of economies of scale obtaining in this industry and may provide an economic production base for entry into the international market.

Notwithstanding the political and economic implications of such an approach, the regions of Latin America and the Middle East may be used for illustration. In planning future development in Latin America a number of large-scale capacity plants and petrochemical complexes may be conceived as indicated for plastics, synthetic fibres and nitrogenous fertilizers products.

In the Middle East on the other hand, economically feasible petrochemical complexes centring round nitrogenous fertilizers may be envisaged.

It should be emphasized that these estimates of potential consumption, as was mentioned above, are made under restrictive assumptions; they are not firm projections of demand and are used only to indicate an order of magnitude. More extensive research would be required to ascertain the level and composition of demand for these products for individual countries and regions. This may require, besides projections based on aggregate parameter, such as national income and population projections based on important end-uses : building construction, transportation, pipes for irrigation and

			fer	vernous tillsers	Synthe	tic rubber	Synthetic Abree	
	1955	1960	19 <b>53-</b> 19 <b>59</b>	1961- 1962	1959	1963	1951	1961
		6	Percentage)					
Western Europe	41.8 0.7 18.4 12.6 10.6 8.5 3.2 0.9 3.3 100.0	54.3 5.0 7.9 7.0 11.5 (4.3) 2.2 3.4 1.4 7.3 100.0	33.7 n.a. 28.7 7.3 18.9 3.7 0.3 7.3 	31.2 3.1 19.9 5.3 30.7 (1.0) 4.8 0.7 4.2  100.0	48.7 3.0 8.9 12.1 14.7 (11.1) 3.5 5.7 0.5 2.2 100.0	49.7 7.6 5.7 12.4 12.9 (10.4) 3.5 3.2 0.8 4.2 100.0	39.6 0.2 9.1 22.7 0.6 3.8 21.6 2.3 	59.9 3.0 5.7 8.9 8.6 (0.5) 6.4 4.1 3.5 

TABLE 4. SHARE OF MAJOR REGIONS IN TOTAL IMPORT OF SELECTED PETROCHEMICAL PRODUCTS

Sounce: " Recent trends in production, consumption, trade and end-uses in selected petrochesnical products ", paper prepared by the United Nations Centre for Industrial Developmen (see paper 1 above). Estimate of potential consumption in latin america, 1975 selected petrochemical products

(In tons)

	Consumption 1962	Present capacity		consumption 975
		1963	A	8
<b>Pla</b> stics				
Polyvinyl chloride		28,000	125,000	200,000
Polyethylene *	a	22,000	140.000	230,000
Polystyrene *		26,000 b	60.000	100,000
Others			225,000	370,000
TOTAL PLASTICS	155,000 ('59)		550,000	900,000
Synthetic fibres . Nitrogenous fertilizers (N)	31 <b>,500</b> 3 <b>70,00</b> 0	48,000 500,000	135,000	200,000 ).000

SOURCE: "Recent trends in production, consumption, trade and end-uses in petrochemical products", paper prepared by the United Nations Centre for Industrial Development (see paper 1 above).

• Estimates based on the share of these plastics contained in the projection for 1970 made by the United Nations Economic Commission for Latin America in "La Industria Química en América Latina" [E/CN.12/628], 1962.

Includes capacity for styrens.

#### POTENTIAL CONSUMPTION IN THE MIDDLE EAST, 1975

(In tons)

	Consumption 1962	Capacity	Estimated consumptive 1975						
			A	,					
Plastics Synthetic fibres Nitrogenous fertilizers (N)	4 600	3,650  140,000	60,000 35,000 1,500	100,000 65,000 ,000					

water mains to mention a few. With respect to the latter the investigation may involve, *inter alia*, the feasible substitutions, both economic and technological, of petrochemical products for competing materials, this being of especial importance in countries and regions such as the Middle East and North Africa that have a relative scarcity of alternative materials and products. Should the feasibility of petrochemical products be established, additional measures 'may be required, including the development of institutions, policy measures for promoting consumption, and the development and adaptation of these products to new applications.

As the above data indicate, an important outlet for potential petrochemical exporters may be the major consuming centres, particularly western Europe, which is not only a major consumer but also a major importer for a number of petrochemical products. This would be of interest to potential exporters from North Africa and the Middle East. However, the progress of western Europe towards economic integration poses an important adverse factor for new entrants from outside the region and securing a market in this region may have to be envisaged through the institution of multilateral or bilateral trade agreements. Markets ouside the economically advanced countries may also be sought, for example in the case of the export of nitrogenous fertilizers to Asia. In this connexion, trade arrangements may be developed between potential exporters from the Middle East and a number of countries of Asia.

Another outlet for petrochemicals may be found in centrally planned countries. Trade between the latter countries and developing countries has been developed primarily through bilateral trade and assistance agreements. Table 5 gives the trade for recent years between centrally planned countries and various developing regions and the rest of the world, indicating that the share of the former ranged between 35 and 40 per cent of this trade.

While trade between centrally planned and developing countries has been increasing in absolute terms, it comprises only a small share of the total trade on both sides. Exports from centrally planned economies to developing countries increased from \$400 million in 1950 to \$1,250 million in 1960, comprising 2.7 per cent and 4.7 per cent respectively and for the same years exports from developing countries to centrally planned economies shared 12.3 per cent and 8.0 per cent respectively of the total exports of the former countries.<sup>18</sup>

Through barter and other international trade agreements, further expansion of trade may be envisaged between developing and centrally planned countries. An increasing emphasis in the latter group of countries on the consumer sector may secure additional markets for certain petrochemical products.<sup>14</sup>

The entry of developing countries into the international market poses a number of questions. The importance of economies of scale would dictate the choice of economically large scale operations; this brings into focus the need for local market. As was indicated earlier, the pooling of regional demand may be required to substitute for such a market.

Further, in the short run there are a host of factors that tend to raise production and marketing cost and they may be attributed primarily to the lack of experience on the part of labour and management in new production and marketing techniques and operations. In marketing these products on the international market, the developing countries would have to acquire experience in catering properly for the needs, requirements and business habits of the consumers with regard to type and quality of products, dependable delivery and development of credit channels and services. While the industry is gaining experience in production techniques, management and marketing, direct and indirect measures involving protection and promotion of the industry, at both the national level (including direct subsidies, tax exemptions, etc.) and the international (including technical assistance), may be required over a specified transitional period.

Further, in developing countries additional investment in infrastructure may also be required, and this investment may be substantial and beyond the means available to a single concern. Another important activity that requires additional capital and trained personnel and that may be classified also as infrastructure is that of revearch and development. Here again assistance both national and international may be also needed.

The international market in petrochemicals is controlled by a small number of companies (an oligopoly) and as such poses another set of problems to new entrants. A breakthrough into this market requires a concerted effort in securing and promoting markets, including international trade agreements and strong financial backing. Joint ventures in various forms between developing countries and established petrochemical concerns often provide a solution for a number of these problems, including the supply of experienced personnel for a transitional period, training of local labour and personnel, providing technical know-how and research, experience in marketing techniques and possible access to the international market.

TABLE 5. TRADE OF CENTRALLY PLANNED ECONOMIES WITH REST OF THE WORLD, \* 1960-1962

		-	l'otal
		Expert	Impert
		(Millions o	f US deltars
Latin America			
1960		231.1	307.0
1961		509.8	584.5
i <b>962</b>	• •	695.4	662.3
Middle East			
1960		326.2	338.7
1961		405.0	312.2
1962		441.1	308.2
Asia and the Far East			
1960		718.5	545.7
1961		858.8	589.8
1962		1,001.2	755.6
Africa			
1960		100.6	118.8
1961		159.5	99.1
1962	•••	179.3	109.2
Total developing countries			
1960		1,376.4	1,310.2
1961		1.933.1	1,585.6
1962		2,317.0	1,835.3
Other countries			
1960		2,971.6	3,097.2
1961	•	3,037.9	3,302.1
1962	•	3,229.7	3,372.2
[otal			
1960		4,348.0	4,407,4
1961	•	4.971.0	4,887.7
1962		5.546.7	5,207.6

Sounce: United Nations, World Economic Survey, 1962, vol. II (asias No. 63.II.C.2) p. 88.

\* Including trade with China (mainland).

<sup>&</sup>lt;sup>13</sup> World Economic Survey, 1962, part I (United Nations publication, Sales No.: 63.II.C.1.), tables 1-3 and "General study of exports of manufactures and semi-manufactures from developing countries and their role in development", paper prepared by the United Nations Contre for Industrial Development, for the United Nations Conference on Trade and Development (E/CONF.46/11).

<sup>&</sup>lt;sup>14</sup> The imports of centrally planned countries from the rest of the world have in the past favoured capital goods. In constrast, the export of developing countries consists mainly of primary goods; the share of manufactured products, mainly light manufactures, constituted 6.1 per cent of their export in 1961. See also foot-note 13.

# 4. THE ROLE OF THE DOMESTIC MARKET IN THE DEVELOPMENT OF PETROCHEMICAL INDUSTRIES IN IRAN AND THE NEED FOR EXPORTS

Participants from Iran

#### Introduction

Iran has for many years been desirous of developing a petrochemical industry so as to take full advantage of its very rich resources of hydrocarbon raw materials. Little has so far materialised for a variety of reasons, including the relatively small market existing in Iran, and the difficulty of exporting. As a result, previous studies and projects for installing a petrochemical industry in Iran, and notably plans to make plastics and fibres, have not yet been followed up by the actual building of any such plants.

However, in the past few years, the demand for petrochemical products has grown rapidly, and factories have been installed for converting imported petrochemicals into plastics, synthetic rubber and detergents. This, together with the development of new processes for making petrochemicals, has resulted in the necessity of a fresh approach to the problem of making petrochemicals in Iran. During the last five years the consumption of plastics, synthetic and artificial fibres, detergents and rubbers has been such that if the Iranian economy continues to grow at the rate predicted in the Third Pian (1962-1967), the consumption of these products will be sufficient to warrant their production in Iran from 1967 onwards. A list of these products is shown in table 1.

## I. Present state of the Iranian market

#### A. PLASTICS

Table 2 shows Iran's 1957-1962 consumption of various imported plastics.

In addition, approximately 700 and 950 tons of finished products were imported in 1959-1960 and 1960-1961 respectively. Consequently, the total consumption can be estimated at about 4,850 tons in 1960-1961 and 5,500 tons in 1961-1962. If products with a cellulose, gelatine and starch base are deducted from this total, the resulting figures will be 4,350 and 4,750 tons of plastics of the type made from petrochemicals.

The annual rates of growth of the importation of raw petrochemical-based plastics to be transformed into finished products in Iran are shown in table 3.

The capacity of the plastics transformation industry in Iran has grown considerably in the last few years, particularly as far as the PVC transformers are concerned. Surveys made in 1960 and 1962 all mention an existing state of over-capacity. This over-capacity was due to a general slowing down in the rate of growth of industrial activity in Iran in 1960-1962. However, since 1963 the rate of industrial growth has picked up again, owing to various governmental measures, and the over-capacity

TABLE 1. ESTIMATED CONSUMPTION OF PRODUCTS IN METRIC TONS PER YEAR (AND EQUIVALENT PETRO-CHEMICAL REQUIREMENTS)

	1996	2961/962	1966/9367	1972 1973
lectics	900	5,000	13-16,000	20-25,000
Synthetic	5,000	2,000 27,000	5- 7,000 30-35,000	7-10,000 35-40,000
Velergents	1,800	8-10,000	15-18,000	25-35,000
viergent Alkylate equi	(360)	1,600-2,600	3- 3.680	5- 6.000
ubbers (tota)	8,000	15,000	25-27.000	40-50.000
rathetic equivalent usable		7,000	12-16.000	20-25.000

TABLE 2. IMPORT DISTRIBUTION (RAW MATERIALS AND SEMI-FINISHED PRODUCTS) (Tons per year)

	Cellulose	Capein Gelatine Starch	General Plastics Rods burs etc.	Phenol Urca etc.	Moulding powder	Total
	(1)	(2)	(3)	(4)	(5)	(6)
957-1958	451	28	224	130	2	294
958-1959	358	37	533	150	1	83: 1 <b>.07</b> 5
959-1960	443	26	1,696	260	23	2,44
960-1961	432	59	2,996	354	47	3,881
961-1962	700	39	3,549	274	28	4,590
962-1963	852	23	5,694	71	-0	6,520

is being absorbed rapidly. The vinyl chloride transformation equipment makes up the major part of the total installed capacity. In 1961 it was possible for approximately 4,500 tons of PVC to be transformed in Iran, while the capacities of both the polyethylene and polystyrene transforming industries were below 1,500 tons. These capacities have been expanded to some extent in the past two years.

TABLE 3. GROWTH OF PLASTICS IMPORTS (RAW MATERIALS AND SEMI-PINEHED PRODUCTS)

	 	Y	 	 	 	 	Annual solal * (Joks per year)	Rate of growth (par cont)
1957-1958							326	_
1958-1959							644	96
1959-1960							1,969	207
1960-1961							3,397	72
1961-1962							3.857	15

· Excluding celluloss, casein, gelatine and starch.

## B. SYNTHETIC AND ARTIFICIAL FIBRES

The textile industry has always been a basic activity in Iran. A special effort was made during the Second Plan (1955-1961), and the capacity of spinning and weaving mills was considerably expanded. The cotton industry had a capacity of  $400 \times 10^6$  metres in 1962-1963 and the wool industry a capacity of  $7.2 \times 10^6$  metres. Despite the existing over-capacity, it is expected that the textile industry will expand substantially — between 20 and 50 per cent by 1967-1968.

The present over-capacity is largely to be found in the plants producing cheaper goods. Improvement of finishing techniques, and modifications of plant in order to produce higher quality textiles and in particular textiles blended with synthetic fibres, will do much to improve sales of locally made textiles and reduce imports of finished goods.

In addition, a knitting and stocking industry exists which consumed approximately 2,400 tons of cotton, wool and synthetic fibres in 1960-1961. This industry must be supplied with raw materials, and though domestic production will suffice in some fields, a large tonnage of fibres is at present imported.

For the time being, all the chemical fibres consumed in Iran are imported. Most of the imports are made up of viscose rayon, and the rest consists of acetate rayon and synthetic fibres. Taking all the chemical fibres together, the imports are shown in table 4.

Whereas the available supply of cotton is far in excess of the domestic demand, the same cannot be said of other sectors. It is estimated that by 1967-1968 some 7,000 tons of synthetic fibres and about 30,000 tons of artificial fibres will have to be imported or made in Iran.

## TABLE 4. IMPORTS OF CHEMICALS FIBRES (TONS)

						_		New materials	Paintes	Total
1960-1961.								12,275	9,815	22,090
1961-1962.	•	•	•	•	•	•	•	19,677	6,496	26,175
1962-1963.	•	•	•	٠	•	•	•	25,174	3,004	28,178

## C. SYNTHETIC DETERGENTS

Synthetic detergents have appeared in Iran recently, and the demand seems to be increasing rapidly despite the very high prices demanded. At present Iran's consumption of detergents is about 10,000 tons a year, and it is expected to reach about 20,000 tons by 1967-1968. This means that if a DDB plant is installed, the rate of expansion of soap production will be reduced, and the greater part of increasing consumption will be met by detergents — probably by dodecylbenzes sulfonate, if it can be sold at a competitive price. In fact, in developing countries it is estimated that derivatives of dodecylbenzene will cover about 90 per cent of the consumption of detergents in 1965 and 70 per cent of the consumption in 1970. Assuming 30 per cent in Iran in 1967-1968, this means that a total of 20,000 tons will have to be put on the market. The detergent base content of commercial products varies from 20 to 25 per cent and the production of one ton of detergent base requires about 700 kg. of dodecylbenzene, meaning that the potential demand for sulfonate will be 4,000 to 5,000 tons and that for dodecylbenzene 2,800 to 3,500 tons.

## D. SYNTHETIC RUBBER

Iran does not produce any rubber at present, and the rubber consumed is imported in the form of raw materials or finished products. The total consumption of rubber in Iran is at present 18,000 tons annually. Tyres and inner tubes make up a large share of imports. One tyre manufacturing plant is operated at present in Iran by the Goodrich company. This plant began operating in 1961 and produced 250,000 tyres in 1962. For this output it used about 1,500 tons of rubber (one-third synthetic and two-thirds natural). New tyre factories are expected to go into production in the next two or three years. Tyres now represent 85 per cent of the rubber consumption in Iran. This proportion will probably increase slightly and come closer to world-wide trends, which are between 55 and 60 per cent. It is estimated that the total rubber used by the tyre industry will reach about 30,000 tons by 1967-1968.

The future portion of synthetic rubber in Iranian rubber consumption cannot be estimated precisely. However, world trends underline the increasing utilization of synthetic rubber. Synthetic rubber production possibilities are quite extensive, whereas the expansion of natural rubber production is quite uncertain at present.

It is forecast that by 1965 synthetic rubber will make up 60 per cent of the world consumption. Since Iran is not yet a producer of natural rubber, similar forecasts can be made in its case, and thus it may be estimated that Iran's synthetic rubber requirement by 1965 will be about 18,000 tons.

## II. Economies of scale and prospects for expert

Economies of scale, a major characteristic of the petrochemical industries, do not continue indefinitely with increase of capacity. Once a certain capacity is reached — a capacity which varies greatly from product to product — economies of scale are no longer obtainable with further increase in capacity. At the other extreme, because of the steep rise in unit production costs that would arise, it is not feasible to operate a plant smaller than a certain minimum size.

In the case of Iran, the internal market is such that in several cases the capacity of petrochemical plants will be greater than the minimum economic size. There is no doubt that unit production costs will be considerably lower if larger plants are built, and a market is found for that portion of the products which is left over when the internal market is satisfied.

A study has been carried out by the Institut Français du Pétrole (IFP) for the establishment of a petrochemical industry in Iran. This shows that certain products can be made at sufficiently low cost in Iran to justify their export. Because of uncertainties about export prospects the design of Iran's petrochemical complex has to a great extent been based on the home market, involving only some excess capacities in the initial years of operation, which can be used for exports. The inclusion of plants designed especially for export will of course be taken into consideration if reasonably firm commitments for export offtake can be obtained.

The availability of cheap natural gas and certain petroleum derivatives in southern Iran is considered to justify the erection of plants, oriented towards export markets, in which raw materials constitute a substantial part of production costs.

Benzene, butadiene, ammonia, methanol and carbon are among products which can be considered for production and export.

#### Benzene

The manufacture of 12,400 tons a year of benzene at Abadan has been recommended as part of the plan for satisfying the home market. This benzene can be made very cheaply at Abadan as the special nature of Abadan's operation, involving superfractionation, results in the availability of a relatively cheap  $C_0$  concentrate with an exceptionally high benzene potential.

There should be sufficient raw material available for increasing the capacity of the units; and the additional production, which might be over 30,000 tons a year, could then be exported.

#### Butadiene

Because of the presence of cheap butane in both the refinery gas and in the low pressure well-head separator gases, it is possible to increase the size of the proposed butadiene plant in Iran and export the excess output,

## Ammonia and fertilizers

Markets for nitrogenous fertilizer exist in many parts of the world and there would appear to be very little difficulty at the present time in selling either ammonia or urea.

A preliminary study carried out on the production and export of ammonia and urea in Iran indicates that these products can be produced at a very low cost and delivered to Far Eastern countries at competitive prices.

## 5. SYNTHETIC SUBSTITUTES OF NATURAL MATERIALS THROUGH PETROLEUM FEEDSTOCKS

## D. M. Trivedi, Project Manager, Synthetics and Chemicals Limited, Bembay, India

#### INTRODUCTION

The need for a Conference of this type, bringing together under the auspices of the United Nations participants from most developed and developing countries has long been apparent. Its importance to the developing countries, which are today groping for economic freedom, having reached the first stage of political freedom, will be seen in its impact on the new resources that many developing countries can marshal to relieve the pressures that their growing population exert on their limited or otherwise undeveloped resources. Its effectiveness will be measured by the degree to which the conclusions of this Conference help the developing countries to mobilize these new resources in the most scientific manner and at the lowest possible costs to meet their basic needs, and by their impact on the future steady improvement in their living standards.

For India the deliberations of this Conference will be of great significance, for the Indian Fourth Five Year Plan is now under formulation and in about a year it will begin to be implemented. Under this plan an effort will be made to orient the chemical industry towards petrochemicals. The papers from Indian technicians submitted at this Conference will indicate the scope and dimensions of this large programme and confirm the significant strides to be made for the first time in India not only to develop the Chemical industry on a large scale but to enable it to take its due place in the promotion of the national economy.

Recognizing the importance of the petrochemical industry, the Government of India have assigned top priority to the development of five petrochemical complexes in different parts of the country, viz. at Bombay (Maharashtra), Koyali (Gujarat), Madras, Barauni (Bihar) and Haldia (West Bengal). The total investment estimated for these five complexes is approximately 5,000 million Indian rupses (approximately \$1,000 million) consisting of about 50 per cent in plants, about 20 per cent in utilities and off-sites and about 30 per cent in production and fabrication of plastic and elastomeric materials. The breakdown for individual items of petrochemicals for which capacities are proposed to be developed is given in annex I.

The figures given in annex I are subject to some reservations as the final data for the Fourth Plan area of yet firmly established. In their effort to organize the petro-

chemical complexes along the proper line, and in a way that is consistent with the needs of the economy and petroleum prospecting and refining within the country, the Government of India have invited several foreign specialist teams to India to study the problem at first hand in the context of Indian conditions. Foremost of these is the team deputed by the French Petroleum Institute, Japanese petroleum interests have now deputed another team to report on the over-all possibilities. It is natural that for a complex such as petrochemicals any change in one direction would influence patterns of production significantly. The figures in the annexe must accordingly be treated as tentative and subject to changes in the light of further expert studies.

#### BASIC QUESTIONS

The basic fact is, however, that the petrochemical industry in India is now earmarked for development on a big scale, but on more or less traditional lines. The purpose of this paper is not to review these normal developments, which are expected to be covered by other papers, but to highlight some pertinent questions and to seek their practical solutions.

(a) Do these programmes based on traditional lines moet the basic needs of India?

(b) is the development adequate or could it be developed on more purposeful lines to meet the growing needs of the people and secure for them a higher standard of living?

#### PREMARY HEED

The primary need for India today is cheap and abundant food for its extremely large population, which now stands at 460 million and is increasing at the rate of some 12-15 million people a year. The need for food would include the supply of fats as well as regar. Is order to improve the standard of living there is also a need, second only to that for food to provide abundantly and cheaply the large volume of fibres required for elething such a large population. In India, by and large, as affort is made to these needs through the utilization of land resources for food crops and each crops such as a cotten, jute, sugar and clieseds, and also through the use of forest and other agricultural residues. It is clear then that in the absence of other resources India's only hope would lie in the land and in the manner and degree of its husbanding and exploitation.

## PRESENT POSITION

To support India's large and growing population the land resources total some 800 million acres, of which only 125 million acres are under forests (i.e. some 14-15 per cent). About 320 million acres represent net sown area. The following data will reveal the important statistics of land and its utilization:

																Million	acru
Total land						,											n
Area under for	ests.											•		·	•	12	-
Not sown area								•	•	·			·	•	·		
Area sown mo	na th	-			<u>.</u>	•	•	•	·	`	•	•	•	•	·	32	
Total cropped		_			• •	•	·	•	•	·	•	·	•	·	٠		0
Total ant index	and a	•		٠	•	•	·	٠	·	·	•	٠	٠	٠	·		0
Total not irriga				•	.:	٠	٠	٠	·	٠	٠	٠	٠	•	•	•	0
Total irrigated				re		Ċ.	0		D)		•			•		1	0
Area under:										( 19		line In		<b>100</b>	,	irrig ( million	and arres
Food grains.						•					3	10	.0			6	۵
Jugar anno .												5	2			1	-
Olieeede	• •										1	33.	Õ			12	•
Cotton.											1	19	5			2	
<b>Jule</b>	• •		•									2				<b>4</b> .	<b>•</b>

The above land resources provide approximately 80 million tons of food at present, where more than 120 million are required and, in addition, also supply annually about 8 million tons of sugar (as gur), about 5.5 million bales (of 392 lbs. each) of cotton, about 7 million tons of oilseeds and about 8 million bales (400 lbs. each) of jute and other bast fibres. As much as 70 per cent of the Indian population today subsists on the land. A rapid look at the above figures would at once show that the productivity of land is very poor and often as low as only 30 per cent of the average yields in other areas of the world. With such depressed conditions of agriculture, inadequate irrigation and fertilizer input, poor tools and implements, seasonal raine and floods, unscientific agricultural practices and almost 3/4 of an acre per capits of land, the problem of improving agricultural productivity is one of huge dimensions in terms of investments in mod farms, fortiliner factories, massive irrigation subsmes, scientific training of farmers and a country-wide educational system for millions of farmers, a purposive mass communication effort on the farms, and the provision of cheap and effective farm tools, map electricity and bottor hygionic conditions of living. not to mention remunarative form priving policies, qu postation of produce and the urgent need for p manirel. In spice of the trousendous effort th a control. In spite of the tremendous effort that has a going an far last thirteen years in India in the form a fre-year plane on the agricultural front, the m of providing an adequate supply of field and of the millions of propie in Jude has continued ) fut the mil to be a very difficult case, as can be such from the st iert de a minimum everage 5 mil ine the of feed

grains annually, at a cost of over 2,000 million rupees, and also cotton, wool and other fibres equivalent to 1,000 million rupees a year. Not only are many areas of the country undernourished today but in some areas this year there have been persistent famine conditions. Even the present level of nutrition in India is based on a potential of only 2,000 calories *per capita* and only sixteen yards of clothing per year. These standards are nowhere nest the average levels reached by the developed countries.

Finding alternative resources which can be quickly husbanded and controlled and thereby releasing more land for food which cannot otherwise easily be synthesized must be the objective of any national programme. The Indian Government is conscious of this need and the massive investment in petrochemical output proposed for petroleum refining and prospecting is the result of this deliberate policy, the objective of which is to improve transport, increase the energy resources of the nation and provide more raw materials for industrial development. However, the effectiveness of this programme has to be judged by the extent to which these outputs help to supplement the resources available from the land and thus relieve pressure on the land for those items which would otherwise have to be procured out of land alone. It is the primary object of this paper to examine this dilemma by illustrating the problem of natural v. synthetic fibres, natural v. synthetic rubbers, and natural v. synthetic fats and natural v. synthetic paper.

#### NATURAL J. SYNTHETIC FIRRE

India's basic fibre is cotton. Almost 20 million acres of land are used to produce about 5 million bales of cotton (i.e. approximately 1 million tons). In addition to this, over half a million bales of cotton have to be imported, representing about Rs.600 million to Rs.700 million of foreign exchange expenditure annually. This imported variety is a long staple cotton for which Indian conditions are not quite suitable. It is partially to meet this need that the Indian man-made fibre industry is being developed. The 1962 production of man-made fibre in India was about 134 million pounds, consisting of:

																	Million Ib.
Viscoss rayon and	80	et:	)ie	n	Ŋ	<b>Pin</b>											62.5
Viscos rayor and	80	oti	110			) de la	•	٠	٠	•		•	•	•	•	•	71.0
Non-cellulosise.	·	·	٠	•	٠	•	·	٠	·	٠	•	•	•	•	•	•	0.5
																	134.0

This works out to a per agoins consumption of manmade fibre of only 0.3 lbs. per year in India, as compared with about 2.80 lbs. per capits world consumption. Computed on this basis, Indian requirements of manmade fibres (for 450 million people) would be of the order of 1,150 million pounds, that is, about 600,000 tons of fibre.

The proposed targets for the man-made fibre industry in the Indian Fourth Pive-Year Plan break down as follows (1976-1973):

	Capacity (In Iona)	Antisipured production (In sone)
Cellulosics		
Viscose fliament yars	60.000	60.000
Viscoss type cord yarn	17.500	17.500
Viacoas staple	90,000	90,000
Acetate yarn and staple	15.000	10,000
Non-cellulosics	182,500	
Polyamide yarn and staple	20.000	10.000
Polyester staple	20.000	10.009
Acryites	20,000	19,990
Polypropylens, polyvinyl aleohol fibre stc.	20.000	10.000
	\$0,000	
GRAND TOTAL	262,500	217,500

As compared with the production rate achieved in 1962. the 1970-1971 anticipated production represents an expansion of over 300 per cent and almost four times the capacity, and at this level it will represent 30 per cent of the per capita world average. However, it will be seen that of the total man-made production over two thirds or 70 per cent represents cellulose based fibres and only one third or 30 per cent is non-cellulosic fibres. The cellulosic fibres require for their production cellulosic raw materials, viz., wood cellulose, bamboo, bagasse and other grasses. However, owing to the inadequacy of India's forest area, which is only 14-15 per cent of the total land as compared with the normally desirable ratio of between 25 and 30 per cent of the total area in any country, almost all viscose fibres are at present made from imported wood cellulose costing substantial foreign exchange. The large viscose target without adequate cellulose resources from indigenous sources would naturally lend itself to perpetual foreign exchange problems as land for the development of bamboo and other materials is scarce. Admittedly some progress is being made in the utilization and development of bamboo and bagasse for viscose pulp manufacture, but in this case the same sources are competing with the requirements for paper and newsprint, Indian consumption of which is going up steeply. With the large and growing sugar industry, the abundant availability of bagasse as a substitute material would help this problem, but in the Indian context of location of the sugar industry in the farm areas and the total inadequacy of rail and transport facilities, most of the bagasse produced is at present used as a source of energy for power and steam for the sugar mills. If coal could be made readily available to the sugar mills at the same cost of bagasse, as much as 1 million tons of good pulp could be reclaimed from the 3 million tons of bagasse obtainable at the present rate of sugar production. However, this is not now in the realm of the practicable. The planning target for cellulosice should therefore in all fairness take second place to larger production of non-cellulosic fibres.

Amongst the non-cellulosic fibres the fashionable names at present are nyions and polyesters both of which, though very good clothing material, are extremely expensive fibres by Indian standards. While therefore their development in India in bulk to meet the needs of a

more well-to-do cross-section of society cannot be ruled out, their acceptance for the mass market even as blends with cotton would still be prohibitive unless they could be produced in extremely large volume and the technical and royalty costs brought down sharply. This unfortunately is unlikely at the present moment. The warm tropical conditions in India for most of the year may preclude large-scale use of these fibres in spite of their superior wash-and-wear characteristics. For the same reason, poly-propylene fibre, the development of which has just begun, may need a great deal of promotional work before it becomes at all so accepted. This would leave another important fibre which closely resembles cotton in its characteristics, namely polyvinyl alcohol fibre. The properties of polyvinyl alcohol fibre are shown, in relation to other fibres in Annex I. This fibre looks like cotton and has superior strength, abrasion and wear properties. It also has the property of moisture absorption, a valuable asset in cotton and viscose for tropical climates. A fibre of this type developed by and in Japan on a large enough scale deserves serious consideration for mass production in very large size plants even though it is strictly a utility fibre. Since it can be made from ethylene instead of acetylene based on naphtha or petroleum feedetock and spun in a manner similar to viscose by the wet spinning technique in aqueous medium, its mass production would not place a strain on the natural resources needed as raw materials for the paper industry or, in the case of viscose, create an additional foreign exchange burden. From the point of view of cost, it is the changest amongst synthetic or man-made fibres and may in very large size plants come close to and compete with cotton fabrics. A production level of close to 100,000 tons of this fibre would take care of the need for all imports of cotton fibre (one-half million bales) and thus save close to Rs.700 million a year in terms of import exchange alone.

The use of acrylic fibres aboutd be considered in relation to the need for woolless fabrics, and garments in India. The wool produced in India, estimated at about 75 million pounds per year, is of a very coarse type. It is made from animals which are not properly resease and which, for want of land, have very four special gradien fields. To meet Indian meed for high grade weethen flow it is therefore importative to have gradie them which could be simply based on propylene or acetylene derived from petroleum feedstocks. In so far as India's meat production coincides with its by-product wool, any emphasis placed on improved methods of raising of lamb or goat stocks of will help to solve the problem of producing better grade wool fibre. At present, however, it seems an inescapable conclusion that the greatest emphasis must be placed on large-scale production of acrylics and possibly also of cheaper poly-propylene fibre to meet the needs of the people of India for winter garments and to this end the target of 20,000 tons for this fibre appears to be too modest. As the acceptance of cheaper propylene fibre as a wool substitute is very likely, the technical question arises which of these two fibres is preferable in terms of production costs.

The above analysis would show the need for a more forward looking approach in planning petrochemical development in India in view of the limitations on natural resources in the country and consideration must be given to the question of the types of synthetic fibres most suited for Indian conditions and of the volume in which they should be produced in terms of economics of scale. The concept of economics of scale is very relevant to the production of these fibres (as against the present tendency in India to build small-size plants) as well as the production of cheaper large volume petrochemical feedstocks.

## NATURAL V. SYNTHETIC RUBBER

The dilemma presented in respect of fibres is to be seen in glaring perspective in respect of rubber requirements. Only a few years ago India was an exporter of natural rubber even at its production potential of barely 20,000 tons per year. With the planned development of industries, Indian cubber requirements have jumped and are close to 90,000 tons today. By 1965, these are expected to be in excess of 110,000 tons. With the massive investment programme proposed for the automobile industry, the 1970-1971 target for rubber consumption is placed between 190,000 and 225,000 tons. How are these rubber requirements to be met? The present Indian plantation production of rubber is close to 42,000 tons. By 1970-1971 this production is expected to jump to about 60,000 tons, leaving a gap of a minimum of 130,000 tons of rubber, representing close to Rs.300 million of foreign exchange for imports. This amount of natural rubber is at present obtained from the plantation area of over 375,000 acres of valuable land situated in the State of Kerala, which is largely a food-deficit state in India. Since there is a great deal of pressure on land, an effort is being made to produce more rubber in the Andaman Islands in the Indian Ocean. If it is decided to grow all of the natural rubber required, the additional land required will be close to half a million acres. Here is therefore another area of conflict between natural and synthetic resources.

Fortunately, the Government of India are alive to this problem and, as a first stage, a synthetic SBR plant has been built to provide a capacity of 30,000 tons per annum. The basic raw material for this large complex is ethy! alcohol derived from by-product molasses of the sugar industry. However, this still leaves a big gap, which must be met with more synthetic rubber. The question is, what kind of rubber? The maze of claims made for the new rubbers, viz., polybutadiene (High cis and Low cis), the poly-isoprene (natural synthetic), the E-P and E-P-T rubbers in their present stage of development and other variants of special synthetics are confusing, the more so when their very recent development admits of relatively limited experience or available expertise on the subject.

Granting that there is considerable scope for improving rubber plantation yields in India by more scientific techniques — and this aspect is not being ignored in India (where present yields are on the average, only 500 lbs. to the acre) — the question still remains how India should proceed to develop new rubbers at considerable cost for the engineering as well as the process know-how. This assembly of experts may possibly help the deliberations by their constructive suggestions for the benefit of the developing countries as in the case of India at least there can be no question of allocating scarce additional land to rubber production when the need for timber, coconut oil and other cash crops like coffee, tea, etc., even aside from food needs, is so great.

## NATURAL V. SYNTHETIC FATS

Reference was made earlier to the utilization of 33 million acres of land for the production of 7 million tons of oilseeds for edible and non-edible fats. Even at this rate and allowing for exports of limited quantities of these oilseeds the per capita consumption in India is very low. Even despite the high cash value of these crops as compared with food crops their production has not increased substantially in volume even when more land has been used for their production. India is therefore compelled to import coconut oil, palm oil and tallow at considerable cost to meet the requirements of the soap and other industries. The question arises how far this problem can be met by purposive planning for production from petroleum feedstocks. Part of the problem in India is very low production of detergents based on propylene tetramer which, necessitates the use of more fatty soaps. The large target proposed for the production of alkylate would therefore reduce the pressure on fatty resources. The soap industry in India consumes over 200,000 tons of non-edible fats. With the growth of industry and the general improvement in living conditions, this consumption will increase greatly, requiring more and more fatty acids. Fortunately in India today the new Cambay and Ankleshwer Crudes, as also crudes from Assam, has a high wax content (8-16 per cent) and these waxes would present a difficult problem of disposal except as cheap fuel. It is known that in the Federal Republic of Germany processes have been developed to convert these waxes into usable fatty acids for the manufacture of so ps and as alcohol for detergent usages. However, not ... ough information or data are available on the subjec to merit serious consideration of the utilization of such waxy residues of

petroleum into useful fatty materials in an attempt to conserve the natural fatty materials for more useful purposes. The developing countries, especially those, like India which have such a problem, could benefit from constructive suggestions from the experts at this Conference.

Finally, the production of sulphur from sulphurbearing petroleum crudes as well as gas has greatly improved the world supply of sulphur. During the Second World War, as well as subsequently at the time of the Korean War the supply of this commodity became very critical. As the Indian resources of petroleum are not, as far as is known, sulphur-based, the reclaiming of sulphur from refining operations would not be possible. However, since India may need to import more and more crudes from abroad, this aspect of planning for sulphur should not be ignored, especially as India's sulphur resources are not known, except the Amzor Pyrites deposits, the extent of which has yet to be properly estimated.

Similarly, as mentioned earlier, the cellulosic resources of India are not at present adequate to support the large and growing demand for paper and packing materials. While the production of jute and other bast fibres and the increasing substitution of plastic materials for craft paper may take care of the growing requirements for packing materials, increasingly large quantities of paper and newsprint would be required to meet the voluminous needs of the Government and of the more than 450 million people in India. The present consumption of paper in India would be close to half a million tons, requiring considerable quantities of imported pulp and special craft papers. Here again the problem seems to be difficult in view of the paucity of resources. It is known that both nylon and poly-vinyl alcohol have been experimented with as paper base material; with what degree of success remains to be seen. The development of cheaper petroleum base stock as paper base material would be of tremendous importance to a country such as India where the limited forest resources even now continue to be depleted to support a growing mass of people on the land.

As India is only entering the field of petrochemicals it can certainly profit by the experience of developed countries. The questions raised in this paper have a certain bearing on the present conditions in India even though they may appear rather abnormal or unique. As in other parts of the world in the context of petroleum refining needs, the requirements of petroleum feedstocks for petrochemical development would be very small of the order of 2-5 per cent - and yet provide a substantial volume of raw materials. As India is expected to reach a refining capacity of over 35 million tons or so by 1975, it can look forward to the availability of considerable petrochemical feedstocks in the future for the solution of some of these problems. It is in these areas that purposeful policies and programmes must be laid down, now when petrochemical development on a large enough scale is under consideration for the first time in India.

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#### ANNEX I

## Targets for petrochemicals

Product	Capacity in production and construction 1963 (in tons)	Total (apucity required 1970-1971 (in tons)	Produce	Capacity In Production and construction 1963 (in tons)	Total canacity required 1970-197 (in tons)
Poly-ethylene	34,000 Nil	129,000 5,000	Other organic chemicals (continued)		
PVC resins	62,000	110,000	Propylene Oxide		10.000
Vinyl chloride for PVC resins .	30 <b>,000</b>	115,000	Methanol	33,000	60,000
Poly-styrene.	30,000	45,000	Ethanol	295,000	315,000
Methyl methacrylate	Nil	8,000	Isopropyl alcohol	27.000	
Poly-acctates	Nil	6.000	Butyl alcohol	16.000	28,000
Vinyl acetate (non-fibre)	8,000	15.000	2-Ethyl hexanol	13,000	16,000
Poly-urethane	Nil	10.000	Pthalic anhydride		13,000
Exposy resins	Nil	2.000	Phenol (excluding use for caprolactum).	12,600	25,000
Nylon .	2.000	2.000	Chlorinated hydrocarbons (CCL <sub>4</sub> and	10, <b>00</b> C	10,000
Polyester .	Nil	3,000	trichloro-othelenes		
		3,000	Ethviene dichloride	25,000	25,000
Synthetic fibres			Maleic anhydride	9,500	9,500
Nylon	5.000	38.000	Aniline.	1,500	3,500
Nylon tyre cord	Nil	28,000	Detergent alkylate		4,000
	Nil	13,000	Formaklehyde		20,000
Polyester	4.000	15,000	Carbon black	20,000	77,000
Poly-acrylonitrile		20,000	Dirucio pentediene	40,000	60,000
Miscellaneous (including PVC, urethane	3,500	20,000	Dicyclo pentadienc.	700	1,200
etc.)	N.11		Vinyl chloride (non PVC uso)		1,000
Poly-vinyl alcohol	Nil	20,000	Poly-butclenes.		6,000
Poly-propylene	NII	10,000	Acrylonitrile (non-tibre use)		5,000
	Nil	10,000	Methyl Ethyl Ketone.		10,000
Synthetic elestomers			Dimethyl terephthalatc.	-	20,000
			Toluene di-isocyanate		10.000
Total synthetic	30,000	120,000	Melamine.		3.000
SBR .	30,000	30,000 *	<u></u>		
Poly-butadiene	25,000	25,000	Others		
Butyl.	NH	30,000	Acetone		
Poly-isoprene	Nil	(7)	Acetone	7,000	22,000
E-P/E-P-T rubbers	Nil	35,000	Styrene monomer	16,500	50,000
Miscellaneous rubbers (nitrile, acrylate,			Caprolactum (fibre grade).	Nil	30,000
neoprene, urethane etc.)		•	Acrylonitrile	Nil	20,000
ther organic chemicals			Benzene	106,000	174,000
			Tokens	6,000	17,000
Ethylene Oxide	12,000	15,000		15,000	17,000
	,	13,000	O- and P-xylene .	18,000	42,000

SOURCE: Indian Investment Newsletter, August 1964.

Author's note : • Additional capacity should be created to obtain economics of scale, to a total of 50,000 tens. • Capacity target of up to 10,000 to he established.

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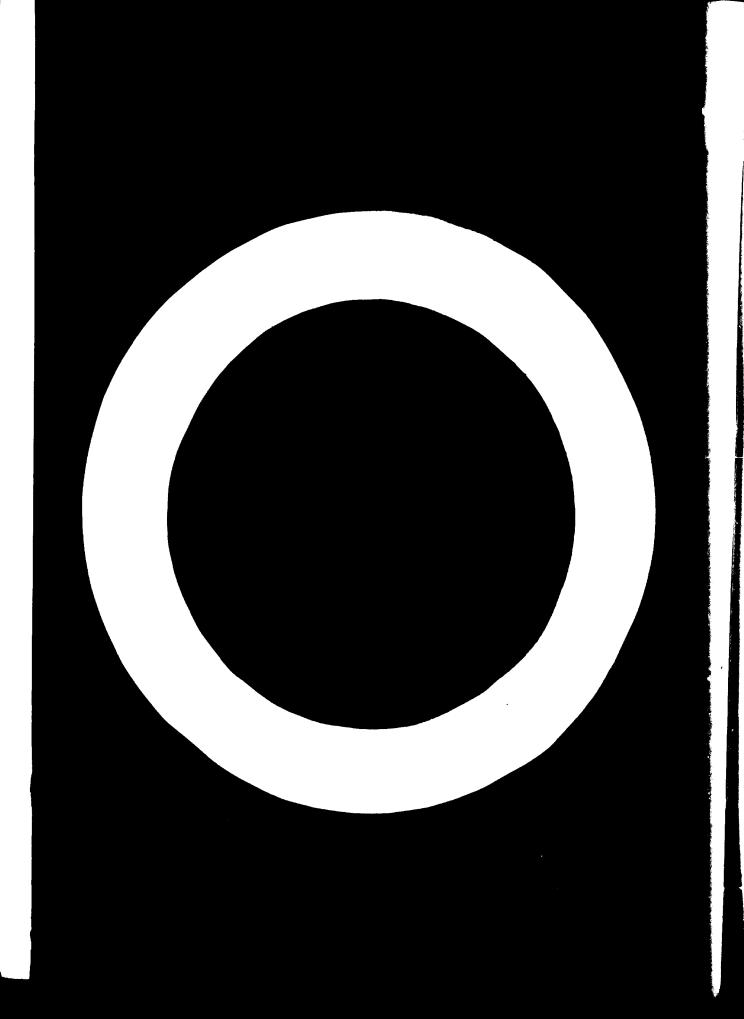
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Ap. gravity	1.15 2.44.1	1.2K 1.144.5	1.14 4.1-5.5	1.36 3.5-5.0	1.17 2.04.8	0.91
	8 24-27 095 % R.H.) 800 % (kg/mm <sup>-1</sup> ) 174 174 174 174 174 170 170 170 170 170 170 170 170 170 170	25-35 10 (R.H. 95 %) 200-1,190 (Good Good Event Freed	23-40 54 (R.H. 95 %) 200 (Lykens) 200 500 600 600 600 600 600 600 600 600 6	19-40 0.4 0.4 (R.H. 65 %) 30-38 30-38 2004 Fair 5004 Good Good	15-25 1-2 (R.H. 65 %) 35-75 (g/dem) 55-05 Good Good Good Good	(depending on type) 25-100 0.05 0.05 0.05 0.05 0.05 (#/den) Evcellent Foor Foor Evcellent

Chapter III

# RECENT TRENDS IN RESEARCH AND TECHNOLOGY IN THE PETROCHEMICAL INDUSTRY



# INTRODUCTORY SUMMARY

The papers in this chapter do not purport to present a comprehensive summary of recent achievements in research and technology, but rather place emphasis only on such work which may have a direct or indirect bearing on petrochemical industrialization in developing countries. In this context advances in cryogenics were described, which enable the liquefaction of natural gas and provide economical transportation and storage. In the case of ethylene production, high severity cracking of naphtha feedstocks gives high yields with minimum coke formation. The price differential of butane and butene feeds has resulted in a trend towards utilization of butane feedstocks by dehydrogenation to butadiene. Processes for isoprene production based on (1) propylene dimerization; (2) isobutylene in Cu refinery streams and (3) acetylene and acetone show possible savings in capital investment and possibility of using inexpensive starting materials.

New trends of acetylene production are by partial oxidation processes. However, a new process based on very high temperature decomposition of hydrocarbon feedstocks in an electric plasma jet reactor indicates possibilities for decreases in price of acetylene.

Recent research and development focus on multiple routes for obtaining a given product to take advantage of different raw materials and to allow flexibility in case of changes in process economics. Among the few major developments in petrochemical research which eithe have been or are soon to be commercialized are (1) new routes to phenol, based on toluene rather than benzene, utilizing the oxidation to benzoic acid, followed by oxygenation using catalytic amounts of copper; (2) oxidative amination of prof. lene to acrylonitrile and (3) new oxidation processes for converting alkyl benzenes to aromatic acids such as the liquid phase air oxidation using acetic acid as the solvent, and a manganese or cobalt catalyst containing added bromide. Among the few major recent developments in organic chemistry which are now affecting petrochemical industry are (1) hydroboration of olefins and other unsaturates for synthesis of terminal alcohol aldehydes, cyclopropane, etc., (2) the use of carbenes in insertion reactions and (3) the syntheses of new olefins and related compounds.

Economics of lower capital investment or lower overhead costs are attributable to processes where traditional intermediates are circumvented and products are obtained in higher yields and purer grades, and also to such new or improved processes whereby new compositions of products are obtained.

Crude oil as a raw material for several chemical synthesis has given impetus to the development of the petrochemical industry.

One of the highlights of the Conference was the report of the Société de Pétroles BP that a considerable number of micro-organisms rich in proteins can grow upon and draw their carbon from the petroleum fractions. Furthermore, laboratory studies on the biosynthesis of proteins from petroleum fractions have made it possible to find culture conditions most favourable for the microbic species selected, which consume the normal paraffins present in certain fractions of petroleum. As a result, a novel utilization of petroleum in the production of proteins was evolved.

The problem of development of petrochemical industries in developing countries is related to the availability of the necessary trained manpower. UNESCO's activity in the training of technologists and technicians for the petrochemical industry is rather recent. Its plans for the petroleum institutes include, among other features, postgraduate training of engineers and research laboratories where every new venture in technological progress can be independently investigated and possibly tried out under local conditions.

## 1. RECENT TRENDS IN RESEARCH AND DEVELOPMENT IN THE PETROCHEMICAL INDUSTRY OF IMPORTANCE TO DEVELOPING COUNTRIES

N. Beredjick, Consultant, United Nations Centre for Industrial Development

#### INTRODUCTION

Before one sets out to deal with the recent trends in research and development in the petrochemical industry, it is perhaps useful to define one's frame of reference. Research has been defined as a studious inquiry, usually a critical and exhaustive investigation or experimentation, having for its aim the revision of accepted conclusions in the light of newly discovered facts.<sup>1</sup>

Whereas this definition may perhaps describe the methodology of research and development in some petrochemical industries, it is necessary to define these activities in a more practical manner and in terms of objectives. Research and development in the petrochemical industry are conducted along two generally broad lines : discovery of new and improvement of existing petrochemical products and petrochemical processes. This division is only functional. Scientists and engineers develop in the laboratory new chemicals from petroleum and matural gas raw materials or develop new or improved methods of synthesizing chemicals hitherto available economically only from other sources (chemical product research). Experimental laboratory products are successfully scaled up to large bench-scale, pilot plant and semi-works stages and finally to full plant manufacturing (petrochemical process development). Within these two general broad lines, one finds subcategories devoted to various specific needs which a particular concern may wish to emphasize.

Rather than develop a comprehensive summary of recent research and development achievements, this paper will attempt to review only such work as in the opinion of the author bears directly or indirectly on any aspects of industrialization in developing countries. Consequently, many excellent research and development accomplishments will be treated only briefly and in so far as they have relevance to the above objective.

## RESEARCH AND DEVELOPMENT ON RAW MATERIALS FOR THE PETROCHEMICAL INDUSTRY

Hydrocarbons constitute essentially all the feedstock for a refinery with other chemical compounds being present in crude oil only in much lesser amounts. Similarly, hydrocarbons provide most of the raw materials used by the petrochemical industry. Figure 1 shows schematically the conversion of crude oil, an extractive mineral to various petroleum products and hence into processed petrochemicals. The list and variety of processed chemicals from petroleum sources is impressive, particularly so when one considers the limited number of initial raw materials required.

Most of the chemicals listed are available from other sources besides petroleum. An inspection of table 1 is therefore revealing; it indicates the extent to which petrochemistry has replaced coal tar distillation and materials of vegetable origin as a source for chemicals.

TABLE 1. PROCESSED CHEMICALS FROM PETROCHEMICAL SOURCES \*

		Per com Petrochemical
Butadiene.		100
Acetylene		25
Dodecylbenzene		60
Polyethylene.		100
Polypropylene.		100
Synthetic rubber		80
Phenol.		74
Ammonia.		96
Urea.		95
Formaldehyde (100 p. ceni)		95
Acetaldehyde		90
Melhanol.		99
Ethanol.	• • • • •	93
lso-propanol	• • • • •	100
Butanol.	• • • • •	70
Eihylene oxide	• • • •	70 96
Ethylene glycol	• • • • •	92
Propylene oxide		100
Propylene glycol		100
Glycerol		
Acryloniirile.		50
Acetic acid	• • • •	100
Acetic anhydride	• • • •	98
Acetone	• • • •	96
Meihyl ethyl ketone	• • • •	83
N-h1	• • • •	100
ashon totanah lantata	• • • •	100
		85
blorohenene	• • • •	100
litechemen	• • • •	60
• • • • • • • • • • • • • • • • • • •	• • • •	60

F. C. Croxton, Battelle Technical Review, 11; 10 (1962); R. Katzen, Hydrocarbon Processing and Petroleum Refiner, 40; 162 (1961).
 Percentage of each of the listed processed chemicals produced from petroleum or natural gas, 1939.

<sup>&</sup>lt;sup>1</sup> Webster's New Collegiate Dictionary (G. and C. Merriam Co., Springfield, Mass., USA, 1961).

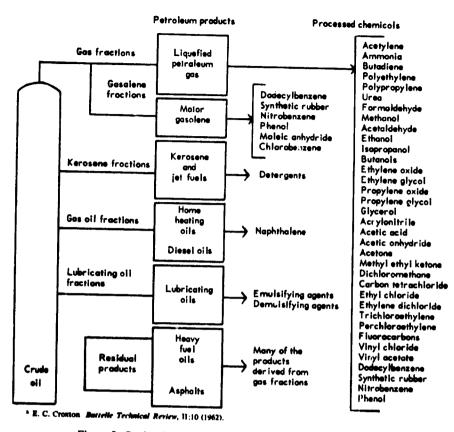


Figure I. Crude oil to petroleum products and processed chemicals -

Basically, the petrochemical industry depends heavily on paraffins, naphtenes and aromatics found in crude oil and on the olefins, acetylenes or aromatics derived therefrom.

#### PARAFFINS

The principle outlets for the light paraffins in petroleum is in the manufacture of olefins. Typically, ethylene is produced by the dehydrogenation of ethane, or by the cracking of propane or butane. Metane, the first member of the paraffin family, is utilized principally in two processes : the controlled oxidation at high temperature with rapid quench to produce acetylene which is later converted to vinyl chloride, acrylonitrile and a number of other organic chemicals, and steam reforming or partial oxidation to produce mixtures of carbon monoxide and hydrogen which can either be used as such, or again be reacted with steam to convert the carbon monoxide to carbon dioxide. The latter can then be extracted, leaving hydrogen for ammonia synthesis or any of a large variety of hydrogenation processes.

The direct use of the carbon monoxide-hydrogen mixture (synthesis gas) is an important and versatile phase in the petrochemical industry. Its utilization includes the manufacture of methanol; manufacture of olefins, alcohols, aldehydes, ketones, etc., by a modified version of the Fischer-Tropach reaction; and the manufacture of higher aldehydes and alcohols by the oxo process. It is worthwhile in this place to emphasize some of the advantageous features of the Sachsse or BASF process utilizing methane from natural gas for the production of acetylene. The process is based on controlled oxidation with a deficiency of the oxidising medium to prevent the oxidation from proceeding to completion. This provides the energy for the main reaction. The over-all reaction is as follows :

$$CH_4 + 1\frac{1}{2}O_3 \rightarrow CO + 2H_3O$$
 (Equation I)  
 $2CH_4 \rightleftharpoons C_3H_3 + 3H_3$  (Equation II)

The reaction temperature is approximately 1,500°C and the products are immediately quenched to 35°C by either water injection or the use of methylpyrrolidone. The advantageous feature of this process is that the byproduct gas contains a substantial proportion of hydrogen and carbon monoxide. These gases, together with nitrogen from an air separation unit, form a suitable basis for ammonia production. This opens the prospects for project integration in a petrochemical complex, i.e., acetylene, synthesis gas, oxo and Fischer-Tropsch reaction products, ammonia and fertilizer production. A more recent process improvement in this field employs redesigned versions of the mechanical equipment (burner and quench assembly) and uses, as selective solvent, liquid ammonia. This version of the process has attracted attention because it can be adapted to the simultaneous production of acetylene and ethylene which offers

economic advantages. It also allows for the use of heavier naphta fractions as feedstock.

Before leaving the subject of paraffins, one ought to mention the recent renewed interest in paraffin waxes. This interest has been stimulated by the need for cheap and convenient sources for long chain primary alcohols for bio-degradable detergents. Thus, in the United States and Western Europe, much industrial research has been done in recent years to develop new processes for cracking paraffinic waxes to terminal olefins and the conversion of the latter to primary alcohols. The Standard Oil Company of California and the British Petroleum Company are known to utilize cracking of slack-wax to produce terminal olefins in the C.6 to C.18 range. The Shell Chemical Company has been using steam cracking of raffinate from furfural extracted cycle oils to obtain such olefins. The British Petroleum Company, Huels and Henkel in The Federal Republic of Germany, and the Standard Oil Company of California, have processes in various stages of research and development for converting such terminal olefins into primary alcohols. A potentially interesting development in this field is the reaction of terminal olcfins with diborane to prepare trialkylboranes. In the presence of hydrogen peroxide in an alkaline medium or by refluxing under oxygen the trialkyboranes are converted into primary alcohols.<sup>2</sup>

It is at this place opportune to mention urea-dewaxing and its application to the manufacture of pure normal paraffins. The dewaxing process which is at present generally used in the industry is based on the removal of paraffins by crystallization, and separation of these paraffins in the temperature range of the desired pourpoint for the oil. This method is effected by low temperature solvent treatment and its operation is independent of the structure and distribution of various paraffinic compounds. It has been known, however, that urea forms crystalline adducts with many linear aliphatic compounds.<sup>3</sup> This phenomenon has given rise to numerous scientific investigations in the United States and western Europe. There are several hundred patents and publications in this area and two technological processes used in industry.4

Dewaxing with urea is competitive with separation by crystallization only when particularly low temperatures (-20°C) have to be used in order to effect crystallization. The application of urea and the formation of the aforementioned complexes is excellently suitable, however, for the separation and preparation of pure normal paraffins, if the low pour-point oil fractions so obtained can also be utilized. Under these conditions, the process has economic merits.<sup>5</sup>

#### NATURAL GAS

The lower hydrocarbons constitute the principal components of natural gas. Natural gas as a raw material for the petrochemical industry and its importance to developing countries is the subject of separate papers to this Conference. It is important, however, to mention briefly in this place a recent technological discovery, the liquefaction of natural gas, which will be of considerable importance to developing countries. This development has added inter-continental mobility to the characteristics of an already popular fuel and raw material, providing a new link between the fuel-surplus and fuel-short areas of the world. It has become possible through advances in cryogenics and through the development of corrosionproof materials to establish economic procedures for liquefaction, transportation, storage and regassification of natural gas. Liquefaction is achieved by reducing the temperature of natural gas to 259°F, its boiling point at atmospheric pressure. At this temperature the liquefied material can be stored at atmospheric pressure in a space only a fraction (1/613) of the volume of the corresponding quantity of gas. However, the storage container must be heavily insulated so that these low temperatures can be maintained continuously.

The significance of this development can only be apprais ed il one bears in mind the vast amounts of natural gas which are commonly flared in oil-producing areas. It has been estimated that 2.2 trillion cubic feet of gas have been flared in Saudi Arabia since oil production was initiated, which represents, for example, more than the total proved reserves in Alaska. Vast amounts of gas are flared in Venezuela and the Middle East alone (3,700 mmcfd). All indications point to the tremendous significance of this technological development. For instance, initial shipments of liquefied natural gas to the United Kingdom in 1964 were estimated at 100 mmcfd. A similar amount for 1965 to the United Kingdom will be followed by 50 mmcfd to France and 30-50 mmcfd to Japan. It is projected that by 1965 ocean transport of liquefied natural gas could range from 1,500 mmcfd to 2,400 mmcfd, with western Europe the largest market. These developments have become possible by significant breakthroughs in such areas as cost reduction, improvement and development of new equipment and techniques for liquification, tanker design, development of insulation materials, and production of storage container materials which do not become brittle at low temperatures. Economic data and cost detail on ocean transportation of liquefied hydrocarbons will be given in a separate paper to this Conference.

#### OLBFINS

Olefins are an extremely versatile source for producing petrochemicals. Of these, ethylene is the olefin of major importance today. Quantities of ethylene consumed by the petrochemical industry in the United States are shown in figure II. The availability of ethylene on a

<sup>&</sup>lt;sup>2</sup> H. C. Brown, Hydroboration (W. A. Benjamin, New York, 1963).

<sup>&</sup>lt;sup>4</sup> F. Cramer, Einschluss verbindungen (Springer-Verlag, Berlin, 1954); W. Schlenk, Fortschr. Chem. Forsch., 2:92 (1951).

<sup>&</sup>lt;sup>4</sup> C. S. Cronan, *Chemical Engineering*, 66:142 (1959); German Patents 1, 105, 090; 1, 104, 101; 1,085,281; 1,015,168, to Edeleanu Gesellschaft, m.b.H., Frankfurt/Main, Federal Republic of Germany.

<sup>&</sup>lt;sup>6</sup> A. Hoppe, Advances in Petroleum, Chemistry and Refining, vol. 9 (Interaciance Publishers, Division of John Wiley and Sons, New York, N.Y.).

<sup>&</sup>lt;sup>6</sup> See below, chapter VIII, 8, Ocean Transportations of Ethylone and other Basic Intermediates for Petrochemicals.

large scale and at economic costs has led to the development of a number of major petrochemicals. The utilization of ethylene in the petrochemical industry in the United States is shown graphically in figure III, together with the projected growth curves of the various petrochemicals concerned. To meet the rising demand for ethylene, producers in the United States are planning to add about one-third more capacity by 1970. Demand growth has been in the neighbourhood of 1,700 million pounds (11 % for 1963). This has exceeded the expansion in capacity and while it has not overtaxed the existing plants in the United States, it has been responsible for keeping production at more than 80 % of capacity. The present capacity in the United States is estimated at about 8.7 billion pounds per year and is projected to reach a level of 12 billion pounds per year by 1970. This boost in capacity for producing ethylene is based on the increased demand for petrochemical products based on ethylene. These, to mention but a few, are : ethylene-propylene rubber, linear longchain alcohols, ethylene replacing acetylene in the manufacture of chlorinated solvents and vinyl-acetate and, last but not least, the growing demand for polyethylene. It appears likely that in the future, ethylene will supplant the higher priced acetylene as a raw material for a variety of products. Imperial Chemical Industries in England is now building a 40,000 tons per year vinyl acetate plant which will be based on ethylene. Shell and other companies have patent coverage in this area also. In addition, the process technology for the ethylene route to vinyl chloride has improved in recent years. This signifies an expansion in the demand of ethylene dichloride. Monsanto and B. F. Goodrich Companies in the United States have installed expanded units for oxichlorination to produce this material. These markets will spur ethylene growth; polyethylene, however, is providing most of the expansion impetus as can be seen from figure 111. In 1963, 2.4 billion pounds of ethylene went into production of polyethylene and it is estimated that in 1964 this will rise to 2.8 billion pounds in the United States alone. Five-year prospects for both high and low density polyethylene indicate an average growth rate of

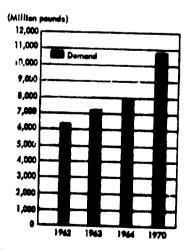


Figure II. Growth of othylene domand for petrochemicals in the United States of America

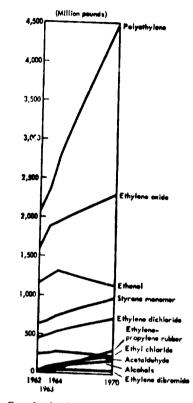


Figure III. Growth of utilization of ethylene in the petrochemical industry in the United States of America

not less than ten percent per annum to 1970. Further impetus in the growth of the ethylene demand will come from ethylene-oxide and styrene, as evident from figure 111.

A recent development in ethylene manufacture has been the utilization of underground storage facilities. This provides a means for surge capacity to ensure that upsets in operation, in either an ethylene-consuming plant or the producing plant, can be absorbed without affecting the operation of the remainder of the system.<sup>7</sup>

The most important advance in ethylene manufacture with regard to developing countries is the use of high severity cracking of naphtha feed stocks. This will be described concisely." In the United States most producers manufacture ethylene by ethane and propane cracking. Consequently, most United States ethylene producers are not concerned with the new process for high severity naphtha cracking. However, naphtha is the raw material for 85 %of the ethylene produced outside of the United States. Naphtha feedstocks have the tendency to coke if cracked as severely as ethane and propane. Consequently most ethylene plants utilizing conventional naphtha cracking are limited to 20-23 % ethylene yields, as evident in figure IV, and produce simultaneously considerable quantities of propylene and four carbon by-products. The new high severity processes for cracking naphtha feedstocks yield more than 30 % ethylene. It is thus

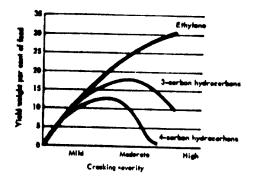
<sup>&</sup>lt;sup>7</sup> Chemical Week, 94(21):67 (1964).

<sup>\*</sup> Chemical Week, 94(20):37 (1964).

apparent that high severity naphtha cracking is the important innovation in ethylene manufacture to come for some time -- an innovation which is likely to become the standard in the next generation of ethylene plants to be built outside the United States. The economic reasons for this merit further elaboration. Suffice it to say that high severity cracking reduces the overall capital investment. It has the added advantage of converting by-products like propylene and butylene into more ethylene. The key to the new process, however, is the elimination of coke formation when cracking naphtha. Most important in this respect is the time-temperature relationships involved in the cracking reaction. For this purpose, the new process uses a radically new design in the high severity cracking furnace. It allows careful control also of such factors as the endothermic heat of reaction during cracking, the heat-input intensity and the mass velocity or residence time of the master feedstock in the furnace. Details of the technical design are described in U.S. Patents 2,525,276, 2,904,502 and 2,914,386, awarded to the Hercules Powder Company. The process has been installed commercially by the Stone and Webster Engineering Corporation for the Daikyowa Petrochemical Company, Ltd. in Japan,<sup>9</sup>

A simplified design of the pyrolysis furnace is given in figure V. A mixture of feed naphtha and primary steam is fed through an injection tube that extends 7 1/2 feet down into a vertical 30 foot long furnace tube. Secondary steam is fed into the furnace tube around the injection tube so that a sheering effect is achieved of the spray at the injection end. Some 2.75 feet below the spray is a main core which extends up from the bottom of the furnace. Additional secondary steam flowing up from this core meets the atomized naphtha and forces it into the annular space between the core and the inside of the main tube, where the naphtha is quickly heated and cracked. Finally, at the bottom of the furnace, the reaction mixture is quenched with water or oil. Further details are given in U.S. Patent 2,638,879 to the Selas Corporation. It is estimated in trade circles that the high severity cracking furnaces are more expensive than conventional furnaces for naphtha feedstock. In addition, the quick quench needed with high severity cracking adds to the cost of the furnace effluent-handling equip-

<sup>9</sup> Ibid.





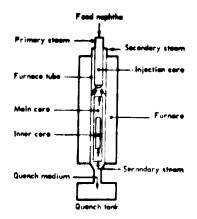


Figure V. High severity cracking of naphtha (pycolysis tube and internal core)

ment. However, both these costs are offset by the reduced distillation costs that result from the reduced propylene, propane, butylene and butane by-products that would have to be separated either for outside consumption or for recycle. Thus, the cost of the furnace is only 10-12 per cent of the total cost of an ethylene plant, while the total installed cost of the entire cracking and quench section of the ethylene plant is only some 25 per cent of the total investment. An interesting feature of high severity cracking is the fact that lighter by-products will thereby disappear. However, benzene does not crack even under severe conditions. It may thus be possible that high severity cracking for ethylene can eventually compete with reforming as a source for aromatics.<sup>10</sup>

Another development in the ethylene field which should be of importance to developing countries is the utilization of ethylene in the manufacture of straight-chain alcohols. This allows for integration of petrochemical projects based on ethylene. Long-chain even number alcohols are of importance in the detergent and particularly in the manufacture of biodegradable detergents, in various heavy duty synthetic detergents and also as plasticizers in thermo-plastics. The process is based on the addition of ethylene to aluminium alkyls to form higher aluminium alkyls which ar ; oxidized to aluminiumoxides and hydrolysed to the corresponding long-chain alcohols. Atomized powdered aluminium is first activated by grinding in a ball mill and a suitable solvent. The activated slurry is then hydrogenated with dry 90 percent hydrogen under pressure. During the hydrogenation step, recycle aluminium triethyl is added from the ethylation step. The first product is di-ethyl aluminium hydrite which, when contacted with ethylene under pressure, yields aluminium triethyl. Aluminium triethyl is then reacted with ethylene under pressure to produce higher molecular weight alkyls. The growth reaction follows a Poisson distribution giving a spectrum of alkyls from Cs to Css. The resulting aluminium alkyls are oxidized with air, to the corresponding alkexides. Small amounts of by-product esters, ethers, acids and aldehydes are formed in this step. The aluminium alkoxides so produced

<sup>10</sup> Bid.

are hydrolysed with sulphuric acid to yield alcohols and a high purity alum solution. The residual sulphuric acid is neutralized with dilute sodium hydroxide after which the alcohols are washed with hot water to remove sodium sulphate. The crude alcohols are then fractionated into individual fractions or two component blends. The higher melecular weight alcohols are distilled under vacuum conditions. The process was developed by the Continental Oil Company in the United States. The fundamental chemical research was done by Professor K. Ziegler in the Federal Republic of Germany. The original plant built by the company in Lake Charles, Louisiana, had a capacity of 50 million pounds per year and has been recently expanded to 100 million pounds per year. In addition, the Ethyl Corporation in the United States is in the process of building a unit with an estimated capacity of 50 million pounds per year and in the Federal Republic of Germany the Condea Petrochemie Gesellschaft m.b.h. is constructing a plant with 100 million pound per year capacity.11

Another important new process utilizes ethylene for direct oxidation to acetaldehyde (Wacker Chemie process). The major current commercial processes for acetaldehyde ar based on oxidation of ethylalcohol. The oxidation of ethylene directly to acetaldehyde appears to represent a definite economic advantage. The process is carried out by the aid of a palladium chloride catalyst. It is a onestage liquid phase operation. All conventional processes to acetaldehyde involve either an indirect route from cthylene via ethylalcohol, as already mentioned, or the use of acetylene which is inherently a more expensive raw material. There is an obvious potential economic advantage in the direct high yield manufacture of acetaldehyde from ethylene. The details of the Wacker Chemie Process are given in another paper at this Conference. Suffice it to say that the process has encountered commercial success and is in operation in the United States by the Celanese Corporation, in Canada by Shawinigan Chemicals Company, in Japan by Mitsui Petrochemical, Mitsubishi Chemical and others, and in the process of completion in Mexico by Petroleos Mexicanos.

A recent development which would be of interest to developing countries in connexion with petrochemical project integration is the development of a process for the manufacture of vinyl acetate directly from ethylene by the imperial Chemical Industries Ltd. in England.<sup>18</sup> The conventional routes to vinyl acetate are based on either acethylene and acetic acid, or on acetaldehyde and acetic acid. This is another instance of the upgrading of a primary petrochemical raw material, circumventing intermediate steps and intermediate products.

#### PROPYLENE

Until a sew years ago propylene as a petrochemical raw material found its major use in the manufacture of isopropyl-alcohol, in the production of propylene trimer and ustramer for detergent use, for the production of synthetic glycerine, and for cumene for phenol manu-

facture. Amounts required were about 2 billion pounds per year and were easily available as by-products from normal refinery or ethylene producing operations. This situation has drastically changed with the advent of the new isotactic polypropylene material. Polypropylene will be discussed in further detail in other papers contributed to this Conference. Suffice it to say in this place that the large acceptance of polypropylene has created a strong demand for propylene of high purity. The C3 stream from normal cracking operation, which contains between 50-70 % propylene, is not sufficiently pure for polymerization purposes. Thus, increasing research efforts have been going on in the petrochemical industry, in industrialized countries, towards the development of selective propylene producing processes. One such process is the dehydrogenation, by catalytic means, of propane.13

The C<sub>a</sub> fractions from a mixed gas stream is isolated in a relatively simple sequence of processes. It is further upgraded, while containing frequently a substantial proportion of propane. As such, it is a suitable feedstock for most chemical conversion processes. Isopropylalcohol is one of the major chemicals produced from propylene by the indirect hydration reaction using sulphuric acid. This technology is well established and will not be described in any detail. A more recent process for the production of isopropyl-alcohol utilizes a direct hydration route. Propylene and water are pre-heated and then reacted under a pressure of 200 atmospheres over a solid acidic catalyst. The catalyst contains tungstic oxide in conjunction with zinc oxide. The operating temperature is 200-240°C. The reaction proceeds partly in the liquid and partly in the vapour phase. A 12-15 % aqueous solution of isopropyl-alcohol is produced. The conditions of operation in practice require a compromise: a high temperature and pressure assist in maintaining a high conversion to alcohol; however, under these conditions an undesirable amount of polymer is formed and therefore a careful regulation of temperature, pressure and water to propylene ratio is necessary.

A recent development of potential significance to developing countries is the commercial application of an oxidation process to isopropyl-alcohol whereby hydrogen peroxide is manufactured. This process can compete successfully with the alternative processes based on inorganic or organic raw materials. Isopropyl-alcohol is oxidised with pure oxygen in the liquid phase at 90-140°C and a pressure of 3-4 atmospheres. The reaction mixture is diluted with water and distilled to remove acetone and unreacted isopropyl-alcohol. The hydrogen peroxide is recovered as a 6-10 % aqueous solution contaminated with organic impurities.

Hydrogen peroxide so produced can be utilized in a novel process for the preparation of glycerine from propylene. The conventional process for the manufacture of synthetic glycerine uses the hot chlorination procedure for propyleue, to give allyl chloride. This is reacted with hypochlorous acid to give dichlorohydrin. The dichlo-

<sup>11</sup> Chemical Engineering, 69(10):80 (1962).

<sup>&</sup>lt;sup>10</sup> Chemical and Engineering News, 43(13):53 (1964)

<sup>&</sup>lt;sup>18</sup> G. F. Hornaday, F. M. Torrell and G. A. Mills, Advances in Petroleum Chemistry and Refuting, 4(10):451 (1961), c.f. Bid., tables VIII and DX, p. 483, 484 (Interscience Publ., Inc., Division of John Wiley and Bon, New York, N.Y.).

ronydrin is converted with lime to epichlorohydrin and the latter is hydrolized with sodium hydroxide to glycerine. (See equations III, IV and V.) This technology is well established and will not be elaborated here. The more recent commercial process for synthetic glycerine has an economic advantage in that it eliminates the use of chlorine which is only wasted as unwanted calcium and sodium chloride in the final stages of the process. This process is based on the oxidation of propylene to acrolein

in the presence of solid copper oxide catalyst. The reaction is carried out in the presence of steam and at a temperature of 300-400°C. The resulting acrolein is reduced to allyl alcohol by an excess of isopropyl-alcohol in the presence of a catalytic mixture of magnesium and zinc oxide. The resulting product is treated with hydrogen peroxide in the presence of tungstic oxide catalyst. By this means the allyl alcohol is hydroxilated to give glycerine. (See equations VI and VII.)

 $\textbf{CH}_2=\textbf{CH}_{\textbf{--CH}_3}+\textbf{Cl}_3 \rightarrow \textbf{CH}_3=\textbf{CH}_{\textbf{--CH}_3}\textbf{CH}_3+\textbf{CH}_3$ (Equation III) Propylene Allyl chloride o 1 + HOCI Ca(OH), (Equation IV) -CH---CH<sub>4</sub>Cl + . 'CH,(OH)---CH(Cl)---CH,Cl Epichiorohydrin Dichlorohydrin NaOH Снон-снон-снон (Equation V) Givcerine + H<sub>1</sub>O<sub>2</sub> CH1 - CH--CH10H i-Pr(OH) ---- CH. -- CH--- CHO (Equation VI) Allyl alcohol Acrolein ↑ + O. CH, -- CH---CH. (Equation VII) Propylene

Figure VI. Propylene to glycerine

A developing country building a petrochemical complex which would produce amongst others, propylene, has an attractive route of utilizing some of its production in the manufacture of isopropyl-alcohol, acetone, glycerine and hydrogen peroxide in an integrated project. Such a petrochemical complex has industrial ramifications extending beyond the production of the four main products mentioned. Acrolein, allyl alcohol, in addition to hydrogen peroxide, isopropyl-slcohol and acetone, are all industrial products with substantial fields of their own merit.

One of the significant achievements of petrochemistry in the last decade has been the utilization of propylene to prepare cumene and from it phenol. Phenol by the cumene route appears to have almost completely displaced the standard processes of sulphonation of benzene and caustic fusion, chlorination of benzene and hydrolysis with sodium carbonate or the chlorination followed by high temperature steam hydrolysis. In the cumene to phenol route, benzene is alkylated with propylene either in the liquid or vapour phase. The most common process is vapour phase and uses a supported phosphoric acid catalyst. The cumene is oxidised in the presence of a dilute sodium carbonate solution to 35-30 per cent cumene hydroperoxide. The latter is now reacted with a dilute sulphuric solution at atmospherie or slightly higher pressure to give phenol and acetone and some small amount of by-products. It appears likely, however, that propylene will encounter strong competition for this outlet as two new processes for phenol have been developed.<sup>14</sup> One oxidises benzene with sir to produce phenol and the other one uses toluene in a similar manner. These recent developments should be weighed carefully by authorities in developing countries if and when establishing plants for the preparation of phenol.

Butylenes, amylenes and other higher olefins have been reviewed recently with regard to methods of production, patterns of utilization, and their suitability as raw materials for the potrochemical industry.<sup>15</sup>

#### DIOLEFINS

#### Dutadiene

The two most important petrochemicals in this category are butsdiene and isoprene, because of their utilization in the production of synthetic rubber. Synthetic

<sup>16</sup> P. W. Cornel and V. N. Heard, Advances in Petroleum Chambery and Anfaning, 2:3 (1939) (Incornelance Publishers Inc., Division of John Wiley and Ban, New York).

<sup>&</sup>lt;sup>14</sup> Chemical and Engineering News 42(17):56 (1964).

rubber was first developed during World War II. At that time, in view of its urgent requirement, butadiene was produced from ethyl alcohol. This process has since been abandoned in industrialized countries as unable to compete with others on an economic basis. The dehydrogenation of normal butenes, also developed late during World War II, replaced the former process as a source of butadiene. Since 1955 approximately a 100 per cent expansion has occurred in production facilities for petroleum-derived butadiene in the United States. The total capacity has risen to 1.2 million tons per year. The dehydrogenation of normal butene continues as the source of about 55 per cent of the butadicne produced, primarily because of the large capacity installed during the War. Most of the new butadiene plants, however, have been based on the dehydrogenation of normal butane. The principal reason for this trend has been the price differential of butane and butene feeds. One of the advanced processes for dehydrogenation of butanes to butadiene is the Houdry Dehydrogenation Process. The principal feature of the process is the utilization of a chromia-alumina catalyst of high selectivity and long catalyst life. The high yields of butadiene are based on the balancing of the endothermic heat of dehydrogenation with the exothermic heat of combustion of catalyst coke and taking advantage of the principle of heat storage in a fixed bed of catalyst and inert particles. The details of this process are the subject of a separate paper and therefore will not be discussed further.16

#### Isoprene

Interest in isoprene has been greatly stimulated by the recent development of all "cis" polyisoprene rubber on a commercial scale. The existing production facilities for isoprene are based on the dehydrogenation of C.5 olefins, present in cracked gasolene fractions, in plants constructed primarily for the manufacture of butadiene from butenes. Where it is necessary to consider developing new production of isoprene in the absence of any existing facilities, several new processes are worth considering by developing countries:

The Goodyear-Scientific Design process for preparation of isoprene from propylene consists of three steps: propylene dimerization, isomerization, and pyrolysis. Dimerization of propylene is affected by passing it over an

acid-type catalyst. The 2-methyl pentene-1 first formed is isomerized to 2-methyl pentene-2 which is pyrolyzed to give isoprene and methane. An important aspect of the Goodyear-Scientific Design Process is the opportunities for investors with limited capital to build and operate monomer-polymer plants of much smaller size than has traditionally been practical with other synthetic rubber processes. Butadiene-polybutadiene plants are seldom economical below a capacity of 50,000 tons per year; isoprene-polyisoprene can be produced profitably. it is claimed by the inventors, well below half this size. Even at the 50,000 ton per year capacity the investment for a butadicne-polybutadiene complex is claimed to be 20 per cent higher than that of a comparably sized isoprenepolyisoprene complex using the aforementioned process for isoprene manufacture.<sup>17</sup> (See equations VIII and IX)

Another isoprene process which has attracted considerable attention, and may be of interest in areas where the raw material is abundantly available, has been developed by the French Petroleum Institute. Isoprenc is produced in this process from isobutylene and formaldehyde. The process is based on the reaction of  $C_4$  refinery streams containing 10-20 per cent isobutylene, with formaldehyde. The condensation reaction produces a dioxane derivative which is decomposed to isoprene, formaldehyde, one of the initial materials which can be recycled, and water. The isoprene so obtained is of very high purity and thus the necessity for capital investment in purification and fractionation equipment is reduced.<sup>17</sup> (See equation X).

Certain developments make it worthwhile to consider the process for isoprene developed by Societa Nationale Metandotti (SNAM) in Italy. This process is based on the reaction of acetone with acetylene to give methyl butynol (MBI).

The latter is selectively hydrogenated to methylbutenol (MBE) and then dehydrated to give isoprene. (See equations XI-XIII). The raw materials used, acetone acetylene, are becoming cheaper and more abundantly available. One reason is the widespread adoption of the process for production of phenol from cumcne which gives as a by-product acetone. Another reason is the development of the new process for direct oxidation of propylene to acetone. In addition new and advanced techniques are expected to reduce the price of acetylene

<sup>16</sup> See chapter IV, A, 9 below Economics of Olefin and Diolefin Production.

<sup>17</sup> M. Heillin, H. Guerpillon and F. Coussemont, Fifth World Petroleum Congress, Section IV, New York (1999).

VIII)

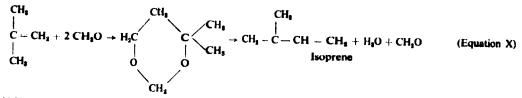
$$CH_{a} CH_{a}$$

$$2 CH_{a} = CH \rightarrow CH_{a} = C--CH_{a}--CH_{a} (Equation 3-Methyl-pattern-1)$$

$$CH_{a} CH_{a}$$

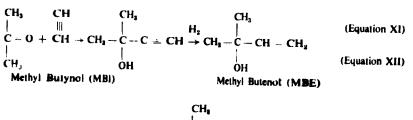
CH\_CH\_CH\_CH\_→CH\_→CH\_=C—CH—CH\_+CH\_ (Repution D) -Methyl-peniene-2 looprene Methane

Pignes VII. Insprene from presultan



(10-20 per cent in C4 refinery streams). 4,4-dimethyl-m-dioxane

Figure VIII. Isoprene from isobutylene



 $-\frac{H_sO}{----}CH_s = C - CH = CH_s$  (Equation XIII) Isoprene

Figure IX. Isoprene from acetylene

in industrialized countries to less than 5 cents per pound;<sup>10</sup> Another advantage claimed for this process is the mild operating conditions in all three stages. This affects the capital investment as the necessary plant can be constructed from ordinary carbon steel. The simple purification technique required to render the product isoprene in a high grade of purity is also an advantage.

Before leaving the subject of diolefins, it is worthwhile mentioning some processes using the latter as raw materials. These may be deemed important to developing countries where a petrochemical complex is built for the production of dienes for synthetic rubber. Any surplus amounts of the dienes could be utilized to produce a spectrum of chemical products. A process which has become of commercial importance recently utilizes the chlorination of butadiene to give 1,4-dichloro-2-butylene. The reaction produces a mixture of both the 1,4 and the 1,2 isomers. The latter is, however, separated and recycled to the reaction mixture to suppress formation of additional amounts of the 1,2 isomer. The reaction products are treated with sodium cyanide in the presence of a cuprous salt. The 1,4-dicyano butylene produced is hydrogenated in succession to adiponitrile and hexamethylene diamine. Hexamethylene diamine is important in the production of Nylon 66.

Another process which is operated on a more limited commercial scale is the treatment of butadiene with sulphur dioxide under conditions of high temperature and pressure. This reaction produces a sulphone which, on hydrogenation, yields tetramethylene sulphone known commercially as sulpholane. Sulpholane is a product of considerable promise as a selective solvent for extractive distillation and solvent extraction processes. It has a very high selectivity as a solvent for aromatics.

#### ACETYLENES

Acetylene competes with ethylene as a raw material in many of its petrochemical applications. Usually the chemistry involved with acetylene is less complex but the lower cost of ethylene as a raw material is a compensatory factor. This subject is dealt with in detail in Professor Othmer's paper. 19 The most common route to acetylene is via calcium carbide and thus indirectly from coal. Until recently, the production of acetylene from natural gas was economical only when no coal or abundant power were available. This situation has changed with the development of partial oxidation of methane for the preparation of acetylene. The Sachse Process and S.B.A. - Kellog Process have been described previously. Another recent significant process utilizing methane from natural gas is known as the Wulff Process. The feedstock is introduced in pairs of furnaces containing refractory tiles. Each furnace operates on a four-stage cycle in which the tiles are first heated and then used to supply heat for pyrolysis, thus making the operation continuous. The partial pressure of the hydrocarbon is reduced by steam dilution and the feedstock is introduced in the furnace at about 0.5 atmospheres pressure. A peak temperature of about 1,500°C is reached and maintained for 3/100 of a second. Thereafter the pyrolysed gas is quenched with water sprays and the acetylene recovered with dimethylformamide.

<sup>&</sup>lt;sup>16</sup> See H. W. Loutzer and C. S. Stokes, *Industrial and Engineering Chemistry*, 53(5):341 (1961), and *Chemical and Engineering News*, 43(3):42 (1964).

<sup>&</sup>lt;sup>10</sup> See chapter IV A below: "Olefins w. acetylene: Competitive rew materials for the petrochemical industries in developing countries".

An acetylene process has been announced recently that may produce acetylene for less than 5 cents per pound. It is based on an electric arc plasma system. The essential feature of the new process is a plasma jet reactor which is capable of reaching 50,000°F. A number of advantageous features are claimed for the process. The reactor is a highly efficient and inexpensive unit; it has no carbon loss and requires no oxygen. It operates at pressures close to atmospheric. This climinates the need for any vacuum pumping equipment and related problems of seals, maintenance, capital costs and additional power requirements. A further advantage is that the purification of the acetylene is simple. Raw gases contain no water or carbon oxide and only minute amounts of solid carbon. Any hydrocarbon feedstocks from methane through the naphthas and even powdered coal or charcoal can be used. Efficiency improves, it is claimed, as molecular weight of the feedstock increases. The ratio of ethylene to acetylene in the product gases may be varied from 0.1 to 1.0 and even higher. An engineering study conducted by the owner of the process (M.H.D. Research Incorporated, United States) indicates that acetylene so produced will cost about 5 cents per pound. This cost figure does not include credit for ethylene or hydrogen by-products which would lower this cost figure even further. The process is now being tested out in a 2,000,000 pound per year pilot plant.\*\*

It is estimated that about 30 per cent of the acetylene used for chemicals in the United States comes from hydrocarbons, principally from natural gas. The major end products based on acetylene are: neoprene rubber, vinyl chloride, chlorinated solvents, vinyl acetate and acrylonitrile. Until 1960, about 86 per cent of the acrylonitrile produced in the United States was based on acetylene. With the recent advent of a process for production of acrylonitrile from propylene and ammonia, it is anticipated that this outlet for acetylene will be diminishing in the long run. For developing countries, the Sohio Process for manufacture of acrilonitrile, based on propylene and ammonia should be of particular significance. It will be described in brief in a later section of this paper.

Substituted acetylenes such as methyl, ethyl and vinyl acetylene, may soon become important petrochemical raw materials. At present, only monovinyl acetylene is used commercially as an intermediate in the production of chloroprene for neoprene rubber.

#### NAPHTHENES

Naphthenes is the common name for a number of hydro-aromatic, cyclic compounds present in crude oil. Of these, cyclohexane is the most important material used commercially. It is utilized for the production of adipic acid, a component in the manufacture of Nylon 66, and also as an intermediate in the production of hexamethylene diamine, the other constituent of Nylon 66. In addition, cyclohexane has gained importance with the rapid acceptance of Nylon 6, which is based on caprolactam. The latter is prepared from cyclohexane via cyclohexanone and cyclohexanone oxime. Details of these processes are given in the paper on nylon.<sup>44</sup> More than 90 per cent of the cyclohexane used in the United States is consumed in the production of Nylon 6 and 66. The remainder is utilized in solvent manufacture. The most common method of manufacture is by fractional distillation from natural gasolene. Some amounts are also prepared in the catalytic reforming of methyl cyclopentene or by the hydrogenation of benzene.

#### AROMATIC COMPOUNDS

Aromatic hydrocarbons are raw materials of major importance in the petrochemical industry. Their availability via petroleum processing has been obvious for an extended period of time. However, only fairly recently have supplies of major aromatic compounds become economically available from petroleum sources. As late as 1949, essentially all benzene for the chemical industry in the United States was supplied from coal tar. The first processing step for the manufacture of aromatics from petroleum is the distillation of crude oil and the separation of straight run gasolenes and other fractions. Recovery is impracticable immediately after this step, as the concentration of naturally occurring aromatics is too low. Straight run gasolene is then subjected to the reforming process. This is a combination of three reactions : dehydrogenation or aromatization, cyclisation and isomerization or dealkylation. The aromaticity of straight run gasolenes varies from less than 5 per cent to about 20 per cent, depending upon the nature of the crude oil and the location from which it was derived. After reforming, the aromatic content is raised to 40-60 per cent. This enables the separation of the aromatics and their utilization for chemicals.

The use of distillation for the purpose of separation of individual aromatics is not satisfactory because of the closeness of boiling points and the problem of azeotrope formation. The separation of the aromatic from the straight run gasolene is done in practice by solvent extraction. Two processes are most prevalent: one uses sulphur dioxide and the other uses aqueous ethylene glycol (Udex Process). Generally speaking, sulphur dioxide extraction is used mainly for the preparation of heavier aromatics. High purity benzene (nitration grade) cannot be produced by sulphur dioxide extraction. Glycol extraction, on the other hand, has proven very satisfactory for the separation of high purity benzene, toluene and xylenes. After the extraction, the mixture of aromatics is passed to a contact clay treater and then to a distillation train where benzene, toluene and xylenes are recovered in separate columns.

A recent development takes a  $C_8$  concentrate from catalytic reforming and Udex extraction containing between 25 per cent and 30 per cent of ethyl benzene and subjects it to a very close fractionation, a process known as superfractionation. This is achieved in a 600 foot column containing 350 plates. Recovery of pure ethyl

<sup>\*</sup> Chemical and Engineering News, 42(3):42 (1964).

<sup>\*</sup> See chapter IV, C helow: "Nylon".

benzene suitable for styrene manufacture is thus achieved. Details of these processes are given in the paper by the Cosden Petroleum and Chemical Company.<sup>22</sup>

An important problem for the petrochemical industry in industrialized countries has arisen with the imbalance between the proportions in which the mono-nuclear aromaties (benzene, toluene and xylene) can be produced by catalytic reforming of naphtha and extraction, and the relative proportion of the market consumption for these products. In this respect, coal tar BTX fractions more closely approximate the chemical end-use pattern as the following volumetric percentages illustrate.<sup>23</sup>

TABLE 2

							Market	Petroleum	Coal ta
Benzene .							65	to	80
Toluene .							20	40	15
X, lene .		•				•	15	50	5
				te	1 A	L	100	100	100

Coal tar aromatic production, however, is intimately linked to steel production. Thus, the situation is governed by economic factors and more particularly by the factor of availability. The aromatics are available from coal to the extent that coal is carbonised. This, in turn, is related to the progress of the steel and the gas-making industry. These industries are not expanding in the industrialized countries in line with the demand for aromatic hydrocarbons. The situation is further "aggravated" by improvements in techniques which have the cumulative effect of requiring less coal to be carbonised per unit of production in these industries. In addition, in some instances, it is economically preferable to leave some aromatic compounds in the gases from coal carbonisation where they have some value as fuel, rather than to undertake the cost and capital investment for their recovery. In short, in 1961-62, of the total United States capacity for aromatics, 79 per cent of the benzene, 91 per cent of the toluene and 97 per cent of the zylenes were derived from petroleum.

To meet the rising demands for benzene without producing additional quantities of toluene and zylene, a process was commercialized in 1961 known as hydrodealkylation. In the hydro-dealkylation process, toluene and hydrogen react to form benzene and methane. The reaction is generally carried out over a catalyst, although thermal hydro-dealkylation can also be used. The product stream is tripped to remove methane and excess hydrogen and then fractionated to separate benzene from unreacted toluene.<sup>54</sup> The principal products of hydro-dealkylation are benzene from tolucne and naphthalene from alphamethyl and dimethyl naphthalene. In some naphthalene processes, a high octane gasolene rather than benzene is taken as a by-product. Until the development of the hydro-dealkylation process, the economies for recovering naphthalene from petroleum fractions were not favourable and supplies of naphthalene from coal tar sources were usually adequate.

The economic situation which has developed in the supply and demand picture of aromatics in the United States may be of interest to developing countries and may effect their own plans for future aromatic production. Most dealkylation process units in the United States were built between 1960 and 1962 when a situation of tight benzene supplies developed. In 1962, however, consumption of benzene levelled off, more Udex facilities were completed and the price of benzene started to drop (from about 34 cents per gallon to its present level of 25 cents per gallon). Since toluene dealkylation costs 7-8 cents per gallon of benzene manufactured, most producers who had the choice cut back on their dealkylation operations. Production was either halted completely or became sporadic, as continuous low rate operation of dealkylation units is not economical. As benzene prices in 1963 remained firm and demand showed signs of resuming its rise, producers of captive toluene began to draw dealkylation units back into use. The year 1964 witnessed a recordbreaking rate at which benzene demand developed. Output of benzene from petroleum sources in the United States is now estimated to reach 625,000,000 gallons for the year 1964, between 50-75,000,000 gallons more than can be obtained through reforming in the refineries. The upshot has been a reactivation of hydro-dealkylation facilities for making benzene from toluene. However, the end of this story is not in sight yet. Toluene is available on the Gulf Coast in the United States at a contract price of about 15 cents per gallon. While there is a keen demand for benzene as a chemical intermediate, toluene's uses are more limited. Thus, the value of toluene is currently lower than that of benzene, to such an extent that it is economic to build a hydro-dealkylation plant consuming toluene and producing benzene. If too many plants, based on this process, are built in the United States, the price of benzene may be forced further down by over-production, while simultaneously the price of toluene may increase, because of its greater usage, to the point at which the conversion becomes scarcely economic. As a matter of fact, many benzene producers maintain that even the present price spread between toluene and benzene makes dealkylation only marginally profitable.35

In summing up, whereas there are some doubts as to the importance of hydro-dealkylation for the purpose of benzene production, this process has established itself definitively for the manufacture of naphthalene. Until 1961, naphthalene was supplied entirely by coke oven operators. Periodic United States shortages were met by imports or, less frequently, by the substitution of ortho-xylene for phthalic anhydride manufacture. Although petroleum based naphthalenes have been consid-

<sup>&</sup>lt;sup>10</sup> See chapter IV. C 6; below "Refining and Petrochemicals Production " by the Costen Oil and Chemical Company.

<sup>&</sup>lt;sup>28</sup> Industrial and Engineering Chemistry 54 (2) : 28 (1962).

<sup>&</sup>lt;sup>14</sup> Chemical Engineering, 68 (20): 46 (1961); and "Bonzene by hydrodealkylatson using the Datel process", chapter IV, A, below.

<sup>&</sup>lt;sup>28</sup> Che nical and Engineering News, 42(29):23 (1964).

ered sporadically for many years, no commercial process existed. A combination of factors served as incentive for the final technological development and actual commercialization of naphthalene from petroleum. It was anticipated that the growth in naphthalene demand would be difficult to satisfy from United States coal tar sources, even if the facilities installed to furnish the full naphthalene potential were utilized by the steel industry. In addition, the booming European economy could not be counted as an import source for coal tar naphthalene and, last but not least, hydrogen was available in sufficient quantities as a by-product from catalytic reforming. This alone was an important condition which did not exist in previous years before naphthalene from petroleum was considered. It is perhaps worthwhile to note the figures which indicate the vigeur with which the petroleum industry in the United States has entered the naphthalene field. Whereas in 1960, 500,000,000 pounds of naphthalene were produced from coke-oven capacities, between 1960 and 1963 the petrochemical industry alone produced 400,000,000 pounds a year of naphthalene based on petroleum.34

#### ASPHALTS

Of the hydrocarbons found in crude petroleum, only the asphalts are of no current interest to the petrochemical industry. This situation may change in the future, however, since techniques being developed for producing chemicals from hydrogen-deficient coal will also be applicable to the low-hydrogen content asphalthenes. For example, application of caustic oxidation to the asphalthenes will produce multi-carbocylic ring acids, which may become valuable pharmaceutical pesticide or plastic intermediates in the future.

## NON-HYDROCARBONS

The major non-hydrocarbon raw materials from petroleum are hydrogen, which is obtained in refinery operations, and sulphur. Sulphur will be treated in separate papers to this Conference.<sup>17</sup>

Hydrogen is used broadly in three areas of chemical processing: hydrogenation and hydrodealkylation processes, in combination with carbon monoxide for oxotype processes, and for ammonia and thereby nitrogenous fertilizer manufacture. The oxo process will be treated in detail in a later section of this paper. Some recent developments in the manufacture of ammonia merit special attention by developing countries, and will be described briefly in this place.

An ammonia plant consists essentially of a gas preparation, compression, synthesis and storage sections. The common material utilized is natural gas, which is reacted with steam and air to produce a purified mixture of nitrogen and hydrogen. After appropriate compression and a heating cycle, the mixture is circulated around a synthesis loop. It repeatedly passes through a converter containing catalysts to produce ammonia.

" See chapter IV, F below: "The Petrochemical Industries" and "Petroleum --- A Major Source of Sulpine".

Conventional ammonia plants involve a number of special pieces of equipment able to withstand the high temperatures and pressures required in the process. Such plants need custom parts which may lead to maintenance delays and replacement problems in developing countries. Recently, by drastic design innovations, new concepts in synthesis converters and the maximum use of standard industrial parts, some equipment manufacturers in the United States have become capable of offering small ammonia plants (capacities of 30-60 tons per day ammonia) which can compete economically with the conventional large plants. The Girdler Corporation, Louisville, Kentucky, by concentrating on pre-assembly of plant components, is able to keep initial plant costs for ammonia low. Details of their development will be found in a paper on this subject at this Conference.28

Significant improvements and innovations in the design of the ammonia synthesis converter are due to the J. S. Pritchard Company of Kansas City, Missouri.29 In a conventional plant, the converter consists of a single pressure vessel containing several beds of catalyst and a heat exchanger. These vessels require elaborate cranes for the vertical removal of the converter's internals because of its height (about 65 feet). Thus, catalyst replacement and routine maintenance is costly and time-consuming. In the new design, this unit has been broken down into five vessels: a heat exchanger and four units containing catalysts. This eliminates cranes and rigging, as the spent catalyst can be removed by vacuum without removing the internal parts. The new vessels are only from 12 to 20 feet high and all work can be done from ordinary portable scaffolds. Such procedures and the additional savings from the use of standard parts, elimination of the use of special tools, techniques and service equipment, should be of special interest to developing countries. For instance, the heat exchanger is placed in a separate vessel. This permits the greater use of standard flanges, gaskets, and other parts. The use of standardized industrial parts reduces down-time, maintenance costs and spare parts inventory. Another advantage is that the smaller vessels are easier to seal, an important consideration for the 3,000-5,000 p.s.i. pressures used in ammonia synthesis units. The company claims that it can supply a 60-100 tons per day plant at an investment of \$20,000-\$24,000 per day ton. This is considered a low figure by knowledgeable circles in the fertilizer industry. With increasing size, the price advantage compared to other conventional plants starts to decrease.

It is perhaps opportune at this place to mention some novel uses of ammonia which should hold the special attention of developing countries. Liquid ammonia has solvent properties that exable it to penetrate the lining fraction of plant cell walls. It is known also to swell cellulose and penetrate its crystal lattice. A recent report describes the treatment of samples of wood of various species, i.e., birch, pine, oak and bass wood, by submerging them in liquid ammonia for about 15-20 minutes. The samples when removed could be bent by the application of very low pressures into circles, double S-shaped

W. S. Poder, Chemical Engineering News, 39(13): 130 (1961).

<sup>\*</sup> Nitrogenous Fertilizers as a Petrochemical Operation.

<sup>\*\*</sup> Chemical and Engineering News, 41(52):38 (1963).

curves, spirals and other various complicated shapes. These shapes retain their new form without clamping as the ammonia evaporates off. In addition, the mechanical properties of the wood undergo very little change. Development of such techniques for woodworking could be of significant interest to developing countries where a conventional woodworking industry has not been established and where sophisticated machinery is not yet in use. Plasticising the wood with liquid ammonia and making it flexible and pliable may enable the manufacture of various forms of consumer items. The technique could be applied to corrugated structures for core stock and possibly to furniture manufacture.<sup>30</sup>

The application of anhydrous ammonia as a cotton defoliant is a new development in agriculture. The defoliating action of the ammonia is simple: it kills the leaf almost instantly. Other defoliants when applied as liquids do not always reach completely into the shielded or lower areas of the cotton plant, as does gaseous ammonia.<sup>-</sup> A further advantage is that the ammonia remaining on the leaf acts as a residual fertilizer in the soil. Recent tests on California and Arizona cotton acreages have established that defoliation can be achieved with 75-100 pounds of ammonia per acre. This amounts to between \$6-\$10 per acre on the basis of prevailing prices of ammonia in the United States.<sup>81</sup>

#### New or improved processes for petrochemical intermediates

The processes described hereafter represent either radically new technologies developed in the last few years or improvements of earlier processes. In each case, traditional intermediates are either circumvented and products are obtained in higher yields and purer grades, or new compositions of matter are obtained by processes heretofore unavailable economically. In each instant some aspects of the processes described allow for economies, whether by lower capital investment, lower overhead costs, or lower cost of equipment maintenance. It is the aim to draw the attention of developing countries to these processes and the possibilities of their utilization in planning the development of a petrochemical industry. This may enable developing countries to avail themselves of the so-called "latecomer advantage" in technological development.

#### LIQUID PHASE OXIDATION

This is a new process which allows the economic production of carbocylic acids, esters and a variety of other derivatives from hydrocarbons by oxidation in the liquid phase at moderate temperatures and pressures. The process has the following characteristics: it is a onestep reaction for oxidising organic substrates; the oxidia-

ing agent is air and the catalyst consists of metal ions (Co and Mn) and a bromine compound. Acetic acid is commonly used as solvent and the operating temperatures are 300-500°F and pressures of 200-500 p.s.i. are utilized. The reaction mechanism is free radical chain, where bromine radicals initiate the reaction and the metal ions propagate it. Termination occurs by carbocylic acid formation or free radical coupling. The process is characterized by a very high oxidation rate and very high conversions of raw materials to end products. A typical procedure as, for instance, the oxidation of para-xylene to terephthalic acid, is as follows: para-xylene together with air. catalyst and solvent are charged to the liquid phase oxidation reactor. The oxidation reaction is carried out either batchwise or continuously. The reactor effluent is passed to a separation section where the off gasses from the reactor are monitored for oxygen content. In the separation section, the terephthalic acid is separated from the solvent which is purified and recycled to the reactor. The product has a purity of greater than 99 per cent. The advantage of this process is that it can operate on a feedstock of mixed xylenes. The mixture of phthalic acids so produced is then conveniently separated by methods of fractional crystallization. A modification of the process produces dimethyl terephthalate directly from parazylene by carrying out the reaction in the presence of methyl alcohol and an esterification catalyst. Commercial installations utilizing this process have been developed in the last few years by the Amoco Chemicals Corporation in Joliet, Illinois, by Mitsui Petrochemical Company and the Maruzen Petrochemical Company in Japan, and by Imperial Chemical Industries in England and N.V. Petrochemie Aku-Amoco in the Netherlands.#

#### New process for production of phenol

The demand for phenol has been continuing at an increasing rate in the last few years because of its extensive utilization in a variety of plastics." Over 90 per cent of the world's production of phenol has been effected with basically three processes: the widely accepted process of cumene peroxidation mentioned in more detail in a previous section, where cumene hydroperoxide is formed by the action of air on cumene and then converted by sulphuric acid into phenol and acetone; the Dow Process in which benzene is converted to chloro-benzene which is treated with caustic soda in the pre- nce of a copper catalyst to produce the sodium phenolate; the latter in the presence of acid is converted to phenol. Thirdly, phenol is produced by the Raschig and modified Raschig processes. In these phenol is obtained via the oxichlorination of benzene (hydrochloric acid and air in the presence of a catalyst). The resulting chlorobenzene is hydrolysed by water and another catalyst.

Two new processes have been developed in the last few years which circumvent some of the cumbersome

<sup>&</sup>lt;sup>40</sup> Course Schwerch Jr., Industrial and Engineering Chemistry, 55:39 (1963).

<sup>&</sup>lt;sup>14</sup> U.S. Potent 3,095,298 to California Chemical Company; and Chemical and Engineering Nowe, 42(5) (1964).

<sup>&</sup>lt;sup>40</sup> D. R. Burney, G. H. Weiseman and N. Fragen, Fifth World Petroleum Congress, Section IV, Paper 17.

<sup>&</sup>lt;sup>20</sup> Chemical and Engineering News, 41(35): 102 (1963).

technology in the aforementioned processes and yield phenol on a more economic basis. With the ever-increasing demand for phenol, it appears likely that new plants to be installed in industrialized countries will use the processes described hereafter.

The Dow Chemical Company has developed a two-step process which starts from toluene and converts this to phenol. In the first step, toluene is oxidised to benzoic acid in the presence of a toluene-soluble cobalt sait at temperatures from 120-175°C. The yield in this step is about 90 per cent. In the second step, the high purity benzoic acid reacts with a copper catalyst at 220-245°C. A cupric benzoate is formed which is thereafter hydrolysed to yield benzoic acid and salicylic acid. The latter decarboxylates rapidly in the reaction medium (water or benzene) to give phenol and carbon dioxide. Product phenol is removed by distillation. Tars and aromatics which may form during the second step are removed from the reaction by extraction with pressurized hot water. Aromatics are recycled and the tars are drawn off. The process can be used to make products other than phenol; for example, para-carbocyclic acids result in the formation of meta-phenolic compounds. When meta-xylene is the basic feed, both para- and meta-phenolic compounds are the product. Other potential products include metacresol from para-xylene, orto- and para-cresol from metatoluic acid and nitrophenols from nitrobenzoic acid.

Benzene is converted to phenol in six steps by a new process developed by the Scientific Design Company. It is first hydrogenated to cyclohexane. The cyclohexane is then separated from the unreacted material and hydrogen, cooled and oxidised with air yielding a mixture of cyclohexanol, cyclohexanone, and unreacted cyclohexane. The cyclohexane is distilled from the cyclohexanolcyclohexanone fraction, and recycled back to the oxidation reactor. The final stage involves dehydrogenation of cyclohexanol into phenol and residual materials. The oxidation of the cyclohexane to a mixture of cyclohexanol and cyclohexanone is carried out with a catalyst of long life and high selectivity. The exact identity of the catalyst is not generally known, although it is believed to be a nickel compound stabilized with alkali metals or a modification of a platinum compound on a carbon black support. This process is of particular interest where integration of petrochemical ventures is considered. As the intermediate for the phenol manufacture in this process is a mixture of cyclohexanol-cyclohexanone, it is feasible that excess quantities of the latter could be utilized for the production of caprolactam which is the monomer for Nylon 6. Thus, both phenol and caprolactam have a common intermediate and the two processes would integrate well under a common roof.

For the sake of completeness, we should mention that the classical Raschig process for phenol manufacture has undergone certain improvements recently which will make it give ground only slowly to the aforementioned newer processes. The original or classical Raschig process is a two-step operation where benzene is catalytically chlorinated in the vapour phase with hydrogen chloride and air, followed by hydrolysis in the vapour phase over a second catalyst. The Hooker Chemical Company has introduced improvements in this process. By redesigning the cooling system for the first stage reactor, recycling dichlorobenzene and utilizing a single distillation system for all products, and a modification of the catalyst for the hydrolysis reaction, pilds of phenol have been obtained in the magnitude of 5 per cent to 90 per cent. This modified process has been installed in Rio Tercero, Argentina, and by the Mitsui themical Industry in Japan.<sup>34</sup>

## PHTHALIC ANHYDRIDE BY THE CHEMISCHE FABRIK VON HEIDEN PROCESS OF VAPOUR PHASE OXIDATION

This process utilizes naphthalene or ortho-xylene in a vapour phase oxidation reaction with air and a vanadium pentoxide catalyst to give a high yield of high purity phthalic anhydride. The naphthalene or ortho-xylene feed is vaporized in an evaporator designed to collect any contaminants in the feed, for disposal. Air for the oxidation reaction is purified and compressed to 5-7 p.s.i. and heated to 660-700°F. Part of the air is routed through the evaporator and the remaining air joins the feed on its way to the reactor. Total air flow is adjusted by a ratio flow control to the amount required so that the feed mixture is below the explosive limit. A specially designed converter, which needs very little labour attendance, is utilized in the oxidation of naphthalene or ortho-xylene. A salt bath cooling agent is used to remove the heat of reaction and this heat is transferred to a steam generating system. The reaction product leaves the converter with the excess air and enters a series of switch condensers of special design where the raw phthalic anhydride in the reaction stream is condensed and collected in the feed tank of the fractionating system. The condensers are arranged so that they can be automatically switched from cooling service to heating service to melt any accumulations of phthalic anhydride on the condensing section. Gases from the separator section of the switch condensers are discharged through a stack or suitable disposal facilities. The raw phthalic anhydride from the feed tank is pre-treated thermally for dehydration and destructive distillation of any volatile impurities. The pre-treated feed containing the raw end-product is then distilled under vacuum whereby pure phthalic anhydride is obtained as a distillate. This can be stored either in the molten state or processed further by solidifying to flakes. Batch distillation allows a fine control of product quality. The process is claimed to have a number of advantageous features.

Some of these are as follows: the use of a greater catalyst volume and greater mass of the converter system and heat transfer medium lends thermal stability to the system. This results in higher yields and also enables the plant to be restarted without preheating after a shut-down of up to 30 hours. The gas and liquid effluents comply with most urban pollution requirements with a minimum of treatment and waste products are easily disposable. Yields are claimed to be at least 5 per cent greater than experienced with other processes. The catalyst has a guaranteed minimum life of 5 years. In practice, the Von Heiden catalyst is claimed to have been in continuous operation for more than a score of years with no reduction

<sup>&</sup>lt;sup>44</sup> Chamboni and Engineering News, 42(17):56 (1964).

in yield. It consists of cylindrical pellets of a special carrier impregnated with  $V_8O_8$  and  $K_8SO_4$ . Maintenance charges, it is claimed, are in the range of 3-4 per cent of plant investment depending on the user's practices. The process allows a choice of orto-zylene or naphthalene depending on the catalysts or combination of catalysts to be utilized.

#### PERACETIC ACID — FOOD MACHINERY CORPORATION PROCESS

The production of hydrogen peroxide in an integrated petrochemical complex has already been mentioned in a previous section. Part of the hydrogen peroxide so produced can be utilized in this process for the preparation of peracetic acid. One of the most important areas of application of peracetic acid is its utilization with batch or continuous epoxidation to produce higher assay epoxides. The latter are important plastic intermediates. Peracetic acid is also of interest for a variety of organic applications, such as hydroxylation, the preparation of amine oxides, sulfones, etc., where its specificity yields products of high purity.

Peracetic acid solutions are prepared by reacting aqueous hydrogen peroxide, acetic acid (glacial or aqueous solution) and a strong acid catalyst. The operating conditions are: vacuum of 50-100 mm. hg. pressure and a reaction temperature of 45-65°C. The residence time varies from 30 to 60 minutes. Over-all yield of peracetic acid based on hydrogen peroxide consumption is about 90-95 per cent. Two typical compositions are produced, one containing 32 per cent by weight peracetic acid in water, and the other 26 per cent.<sup>34</sup>

For safety purposes, continuous distillation of the product as formed from the boiling reaction mixture is practiced. The reactor-reboiler contains a larger than catalytic amount of sulphuric acid (10-20 per cent on the combined weight of hydrogen peroxide and acetic acid). No sulphuric acid appears, however, in the distillate and virtually no make up is required. Build-up of impurities in the reactor-reboiler is prevented by an intermittent purge. The reactor-reboiler is connected to a series of rectifying columns which serve to strip out the hydrogen peroxide and reduce the amount of acetic acid in the product overhead. The acetic acid recovered from the spent solutions is recycled to the generator. The plant embodies a water flood mechanism and sensitive controls for maintaining a predetermined temperature and pressure. In addition, rupture discs designed to relieve at a given temperature are used as safety devices.

It is, in this place, opportune to mention one of the recent uses of peracetic acid. This is in the manufacture of caprolactam by a novel process developed by Union Carbide. Cyclohexane is first oxidised and then dehydrogenated to cyclohexanone. It is then oxidised to caprolactone and converted by ammonia to caprolactam. Caprolactam, as has been mentioned before, is an important intermediate and a raw material for Nylon 6. In this process, the formation of ammonium sulphate as by-product is avoided.<sup>36</sup>

#### PROCESSES FOR THE MANUFACTURE OF VINYL CHLORIDE MONOMER

A new process for vinyl chloride monomer production has been developed by Kureha Chemical Industry Company, Ltd. and Chiyoda Chemical & Engineering Construction Company, Ltd. in Japan. It is based on a mixture of acetylene and ethylene obtained by naphta cracking and has a significant economic feature in that it is economically viable even in small-sized plants. Feedstock for this process is a mixed gas containing about 20 per cent of acetylene and ethylene which is generated by naphta cracking. Chlorine adds to ethylene to produce ethylene dichloride. The ethylene dichloride is cracked into vinyl chloride and hydrogen chloride. The hydrogen chloride then adds to acetylene and gives additional amounts of vinyl chloride.

The gas obtained from the naphtha cracking portion of the plant contains small amounts of impurities such as unsaturated hydrocarbons and tarry materials which affect the catalyst adversely. The gas is therefore compressed and the undesirable impurities removed by scrubbing. The scrubbed gas is then fed to the chlorine addition reactor where ethylene is converted to ethylene dichloride and the ethylene dichloride produced is purified by distillation. The ethylene dichloride is then thermally cracked in a fired heater. After that, the effluent containing hydrogen chloride, vinyl chloride and unreacted ethylene dichloride is quenched and separated. The hydrogen chloride is recycled to the reactor where it reacts with acetylene to give additional amounts of vinyl chl ride. The off-gases containing hydrogen, carbon monoxide and methane from the chlorine addition reactor, are used as fuel for the ethylene dichloride cracker.

The Société Belge de l'Azote has developed a process for vinyl chloride production (N.O.C. Process) which reduces purification and concentration costs for the raw material; acetylene and ethylene produced by pyrolysis of liquid hydrocarbons, i.e., naphtha. The process is based on the direct use of diluted acetylene and ethylene in the pyrolysis gas. The process embodies three distinct stages. In the first stage, acetylene diluted by other gaseous constituents reacts selectively with hydrochloric acid and produces vinyl chloride. Ethylene behaves like an inert gas in this stage. In the second phase, the ethylene is combined with chlorine to give 1-2 dichloroethane and, in the third phase, the dichloroethane is pyrolysed leading to the formation of vinyl chloride and hydrochloric acid. The latter is re-used in the first phase by recycling. The gases such as hydrogen, carbon monoxide, carbon dioxide, methane, ethane and ethylene, behave as inert gases and do not affect the rate of transformation of the acetylene into vinyl chloride. At the outlet of the first reactor, the vinyl chloride formed is separated from the gas by solution in an appropriate solvent from which

<sup>&</sup>lt;sup>28</sup> Persontic acid generator, Technical Data Shest, Department 7-62 F.M.C. Corporation, San Jose, California, United States

<sup>&</sup>lt;sup>48</sup> Chemical Engineering, 71 (16): 85 (1964).

it is later recovered by distillation. The gas, now free of vinyl chloride, is sent still under pressure to a second reactor where the ethylene and chlorine are combined using a catalyst. Under the operating conditions of the process, chlorine does not react with the hydrogen present and it is completely used up for the production of the dichloroethane. At the outlet of this reactor, the dichloroethane is condensed, distilled and then pyrolysed under pressure in the cracking furnace. This allows the collection of the hydrochloric acid to be used directly in the first stage of the process without compression. It is claimed that the vinyl chloride obtained has a purity better than 99 per cent.

## TOLUENE DI-ISOCYANATE

Toluene di-isocyanate is an important intermediate in the manufacture of polyurethane plastics. Its production is based on the nitration of toluene to 2-4 dinitrotoluene. The latter is hydrogenated to the 2-4 diaminotoluene which is then reacted with phosgene to give 2-4 toluene di-isocyanate.

Nitration grade toluene is fed continuously through a series of reaction vessels called nitrators, while sulphuric acid and nitric acid are fed continuously through various nitrators downstream from the first reaction vessel. The mixed acids are heavier than toluene so that in the separators the acid settles to the bottom from where it is sent, in reverse flow, back through the system while the toluene flows forward through the system and is nitrated in stages. Products obtained consist of the desired 2-4 dinitro-toluene in addition to a mixture of para-, metaand ortho-isomers. The reaction mixture flows continuously forward through a series of washing vessels, each followed by a separator.

The washed neutral dinitro-toluene is fed continuously from a storage tank to the hydrogenation reaction vessels, into which hydrogen gas is fed also continuously. From the hydrogenator the mixture of crude toluene-diamine obtained, water, and nitro-amines pass through a series of distillation columns. Here the water is separated out overhead in the first column and returned to the hydrogenation feed system. Pure toluene-diamine is taken off overhead to storage in the second column and the third column recovers nitro-amine and returns it to the hydrogenation feed system.

The purified toluene-diamine is fed from storage along with ortho-dichlorobenzene solvent through a vessel where. by continuous agitation, a homogeneous solution is achieved. At the same time, phosgene is fed to another dissolver along with ortho-dichlorobenzene solvent. The phosgene solution and the TDA solution then are fed into three reaction vessels in series each of which is held at a different temperature to allow the phosgenation to proceed in stages. The HCI gas formed as a by-product in the reaction is absorbed in a water absorber and the residue gas goes through a destroyer unit to decompose all remaining traces of phosgene before vesting in the atmosphere.

The crude toluene di-isonyanets flows from the third reactor to a degassing tank where nitrogen and methane are used to strip the dissolved phosgene and this off-gas flows through a phosgene scrubber for recovery. The reaction mixture is then distilled through three distillation columns in series. In the first, the solvent is stripped off overhead and fed back to the phosgene scrubber; the second column takes off 80-20 TDI product overhead; the third column is used chiefly to recover additional TDI from the residue and recycle it into the second column. The entire process is continuous and is instrumented to insure operation with a minimum of labour attendance. Yields of toluene di-isocyanate average about 75 per cent of theory.<sup>37</sup>

## PROCESS FOR THE PRODUCTION OF ACRYLONITRILE FROM PROPYLENE AND AMMONIA

This process was developed by the Standard Oil Company (Ohio) and is based on the reaction of propylene, ammonia and air or oxygen to produce acrylonitrile. The aforementioned raw materials are introduced into a fluid bed catalytic reactor at about 5-30 p.s.i. and 750-925°F. The cooled reactor effluent is scrubbed in a counter current absorber. The organic materials in the water phase are separated by distillation whereby pure acrylonitrile and acetonitrile are obtained. The light end off-gas is rich in hydrogen cyanide which can be recovered as another valuable by-product.

The important feature of this process is the high conversion obtained on a once-through basis in the fluid bed reactor. Difficult separations and recycling of unreacted raw materials is thereby unnecessary. The catalysts used are based on molybdenum and bismuth salts. An important advantage of the process is claimed in that the absorber operates at essentially atmospheric pressures; so do all the distillation columns. The process is being installed commercially in a plant of the Standard Oil Company (Ohio) and also by the B.F. Goodrich Chemical Company in the United States, and in Japan by Nitto Chemical Industry Company Ltd., Yokohama, and Mitsubishi Chemical Industries Ltd., Mizushi.<sup>88</sup>

#### THE OXO PROCESS

Certain improvements in oxo technology, in recent years, make it well worthwhile discussing in this place. The oxo reaction consists of the catalytic addition of carbon monoxide and hydrogen to an olefinic bond. The reaction takes place at about 150-200 atmospheres presure, and 110-190°C temperature. An aldehyde containing one more carbon atom than the starting olefin is the main product. In most commercial practice, the aldehydes are hydrogenated further to the alcohols in a separatstep. The two-stage operation is known as the Oxo Process. The reaction proceeds under the catalytic action of a homogeneous catalyst, soluble in the reaction media. The most effective known catalyst is cobalt octacarbonile which, under the reaction conditions, reacts with hydrogen to form cobait hydrocarbonile. The latter is the

<sup>&</sup>quot; Toksons di-isocyanste Technical Process Data Sheet — The Leanard Process Co.

<sup>\*</sup> Chemical Engineering Progress, 65 (October 1988).

catalytically active species. In the United States, the oxo alcohols produced commercially are: butyl, amile, iso-octyl, nonyl, decyl, and tridecyl. Propionaldehyde and butylaldehyde are also manufactured. These oxo products require as raw materials such refinery olefins as ethylene, propylene, butylene, heptenes, octenes, nonenes and dodecenes. These are produced in cracking operations or can be obtained as fractions from the products of refinery polymerization of gases from cracking operations.

In the conventional oxo technology, the raw aldehyde leaving the oxo reactor is treated with steam at a higher temperature to convert the cobalt catalyst to a form in which it can easily be separated from the reacting mixture. Etablissement Kuhlmann (Paris, France.) has recently announced a novel catalyst-reclaiming method.<sup>39</sup>

According to this procedure, metal carbonates (magnesium, zinc, thorium) are added to the effluent of the oxo reactor. There they react with the dissolved cobalt carbonyl catalyst to form a metal cobalt carbonyl complex. This complex is insoluble in the oxo product but is soluble in water. Consequently, the complex is extracted with water and decomposed by mineral acids into metal salt and cobalt carbonyl. The volatile cobalt carbonyl is stripped out of the acid solution with the hydrogen carbon monoxide gas en route to the oxo converters. Thus, the cobalt carbonyl is recovered and recycled in one of the converter feed streams without being decomposed.

Except for a recent British patent,<sup>40</sup> it appears that this technique is totally different from those of other oxo processes. As mentioned earlier, in conventional oxo technology the cobalt catalyst is decomposed either by heating it (300-350°F) in the absence of carbon monoxide, or by treating the catalyst in the effluent with organic acid to form cobalt salts. Both conventional procedures have disadvantages. The thermal route is not quantitative and cobalt metal precipitates on the equipment. This necessitates periodic shut-downs for cobalt recovery. The use of organic acids causes corrosion problems and requires adding considerable amounts of unwanted water.<sup>41</sup>

Closely allied to the oxo process is the process for making tertiary carbocylic acid by the reaction of olefins with carbon monoxide, water, and a strongly acidic catalyst (Koch acids or neo-acids). Carbo nonoxide tends to react at the branched carbon. Thus, if the olefin raw material is branched, the product is a tertiary carbocylic acid. Such acids are potential intermediates for a variety of products ranging from drugs to plasticizers.<sup>44</sup> This may explain the renewed interest in some industrial countries in this process. A brief summary of the current

Prench Patent 1,223,381 (to Etablissement Kuhlmann, Paris, France).

40 British Patent 942-542 (to Imperial Chemical Industries Ltd).

line-up of Koch Process acids encompasses the following: pivalic or neopentanoic acid (trimethyl acetic acid) made from isobutylene. It is made by Shell in Europe and scheduled for production in the United States in 1964 by Enjay Chemical Company. The latter also will produce neoheptanoic acid ( $\alpha$ ,  $\alpha$  dimethyl valeric acid) based on 2-methyl pentene-1; neodecanoic acid (mixed branch C 10 acid based on tripropylene), and neotridecanoic acid (mixed branched C.13 acids based on tetrapropylene). Shell Chemical has two more Koch acid products: "vercatic g acid" (mixed branched C.9 acids) based on di-isobutylene and "vercatic 151 g" acid (mixed branched C.15-C.19 acids) based on cracked wax olefins.

The basic technology is covered in the German Koch Process owned by Karl Ziegler's patent firm, Studiengesellschaft Kohle. The successful development of these acids and their derivatives could prove a new outlet for branched olefins. Some of these olefins are now losing ground or have static markets, i.e., isobutylene for butyl rubber, or olefins for synthetic detergents. Thus, although the new acids do not have any firmly developed markets, their versatility has apparently encouraged some plant construction in industrialized countries.<sup>40</sup>

#### RECENT DEVELOPMENTS IN PETROCHEMICAL END PRODUCTS

Needless to say, one of the most significant developments in petrochemical end products constitutes the development of stereoregular poly a-olefins. Organoaluminium complexes, now widely referred to as Ziegler-Natta catalysts, permit the polymerization of ethylene and other 2-olefins to take place at low temperatures and pressures, and hence more economically than at the high pressures previously required. More important, these new processes furnish polyethylene of higher density than was previously possible to produce. The concentrated research efforts of many laboratories, spearheaded by the group of Professor G. Natta, from the Polytechnic Institute of Milano, have led to the development of a broad spectrum of new stereoisomeric polymers. The stereoregularity, linear molecular structure and pronounced crystallinity of these materials generally imparts them with greater stiffness, higher heat resistance, better clarity and improved tensile strength. This subject is covered in detail and admirably well by Professor Natta in a separate paper contributed to this Conference.44

A complete new family of plastics, polyimides, with a temperature resistance equal to that of aluminum has been developed in the last few years.<sup>46</sup> Professor E. S. Marvel and co-workers discovered that one can prepare high molecular weight polybenzimidazoles by the reaction of diphenyl esters of aromatic diacids with aromatic tetra-amines.<sup>46</sup> These polymers in general do not melt, but some are soluble in solvents. When heated above

<sup>&</sup>lt;sup>46</sup> Chemical Wook, 94 (23): 45 (1964) and A. Voorhiss, Jr., J. J. Owan, and J. F. Johnson. Advances in Petroleum Chemistry and Refining, vol 1 (10): 467 (1958) (Interscience Publishers Inc., Division of John Wiley and Son, N.Y.).

<sup>&</sup>lt;sup>46</sup> U.S. Patents 3,059,004 and 3,059,005, and 3,059,605 (to Shell Chemical Company).

<sup>4</sup> Chemical Work, 93:67 (August 10, 1963).

<sup>&</sup>lt;sup>46</sup> G. Netta and G. Crupi, *Recent Trends of Petrochemistry in the Macromolocular Pield*. Chapter III, 3, below.

<sup>4</sup> Modern Plantes, 40: 242 (1963).

<sup>4</sup> H. Vogel and C. S. Marvel, J. Polymer Science 1A: 1531 (1963).

400°C, they become insoluble due to cross-linking. The physical characteristics of these plastics and their resistance to high temperatures make them suitable for a variety of applications as substitutes for more conventional materials. Polyimide fibres have a tensile strength of 4.5 g. per denier at room temperature, retain this strength at 450°C for a long period and remain intact even at 525°C for ten minutes. A polyimide adhesive is effective for stainless steel from -215° to +535°C. Glass laminates made with this resin have an initial flexural strength of 75,000 p.s.i. and retain essentially this strength even after 100 hours at 285°C. Such characteristics have given impetus for development work in industrialized countries for polyimide films, fibres, adhesives, wire enamel, insulatory varnishes, coated glass fabrics and moulding materials.47 The paper of Professor H. Mark and S. Atlas deals with this subject in more detail, and also covers other recent developments in engineering plastics.48

Synthetic fibres, synthetic elastomers, and nitrogeneous fertilizers are important petrochemical end products. The recent trends in these areas and their significance for developing countries are well described in a number of papers to be presented at this Conference. For synthetic fibres, the reader is referred to the papers of Professor Lewis P. Hatch,<sup>40</sup> Hoechst-Uhde International,<sup>40</sup> Scientific Design Company,<sup>41</sup> Staatsmijnen,<sup>44</sup> Asahi Chemical Company,<sup>48</sup> Hans J. Zimmer, Aktiengesellschaft,<sup>54</sup> and others. Recent developments in the field of synthetic elastomers are dealt with in detail in the papers of Dr. T. K. Roy and Professor D. F. Othmer.<sup>44</sup> Technical and economic features of developments in the nitrogeneous fertilizer field are described in detail in the papers of William J. Haude, Samuel Strelzoff, Sr., R. de Picciotto and G. C. Sweeney, Jr., R. M. Reed and C. R. Sloan, and Dr. S. Kodama.44

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<sup>40</sup> Lowis P. Hatch, University of Texas, Nylon, chapter IV, C, below.

<sup>10</sup> D. Thormann. "Development of a synthetic fibre industry, such as nylon-6, in developing countries", chapter IV. D. below.

<sup>81</sup> R. Landau, Scientific Design Co., "Polyester Synthetic Piber Materials for Developing Countries".

<sup>10</sup> L. J. Revallier, Staatemijnen (Dutch State Mines) "Methods for the preparation of caprolactam", etc, chapter IV, D, below.

\* Tsunoda, Japan, Astylic Fibers, chapter IV, D, below.

<sup>44</sup> J. Laub and Hans J. Zimmer, Synthetic Fibres of Polyamidae, chapter IV, D, below.

<sup>10</sup> T. K. Roy, "The news synthetic rubbers", chapter IV, E, below; D. F. Othmar, Synthetic rubber as related to petrochemical preduction in developing countries, chapter IV, B, below.

<sup>16</sup> William J. Haude, The economics of international distribution of analysiness anomenic, chapter VIII, below; "Economics of ananomic production in the developing countries", chapter IV, B, below; A. de Pisciotio and G. C. Sweeney, Jr., Annuesis memories two frees pervolves feederecks, chapter IV, below; R. M. Reed and C. R. Sheen, "NEruges fertilizers as a petrochemical operation", chapter IV, B, below; at. S. Kodama, "Recent transfe of the ammonia industry in Japan", chapter IV, B, below.

#### CONCLUSIONS

It is a difficult, if not impossible, task within the scope of a single paper to encompass the various advances in research and development in the petrochemical industry and the numerous technological processes which may be most appropriate for developing countries. As a matter of fact, this was not the task as set by the author. Rather, an attempt is made to highlight such work in research and technological development which is most likely to be adaptable to developing countries. It is perhaps opportune, even with the danger of repeating oneself, to set forth again the criteria for selection of processes and product technologies for presentation in this paper. It has been the objective of this paper to focus attention on such developments that circumvent traditional techniques, leap-frog unnecessary intermediaries, and give petrochemical products in higher yields and purer grades using processes of lower capital investment, lower overhead costs and enabling various other economies to be achieved. Although the advantageous features of each technology were spelled out before, it may be worthwhile to summarize these briefly.

The use of high severity cracking of naphtha feed stocks is a significant development in the field of ethylene manufacture. Higher yields of ethylene are obtained without concurrent coking of the feed. An additional advantage is the conversion of propylene and butylene into more of the desired ethylene. It was also attempted to show the numerous possibilities for project integration based on ethylene raw materials. The recent process development in the field of long-chain alcohols, direct oxidation of ethylene to acetaldehyde and vinyl acetate, was briefly described. By the same token, in the area of propylene technology, the direct hydration of propylene to isopropyl alcohol, the production of hydrogen peroxide from isopropyl alcohol, and the use of the latter with hydrogen peroxide to obtain glycerine were described.

Three processes in the field of isoprene manufacture were described. Each one makes specific claims which may be appropriate to the prevailing local conditions. The Goodyear-Scientific Design process purports to give a 20 per cent saving on the capital investment for a complex based on isoprenepolyisoprene of 50,000 tons per year capacity over the alternative complex based on butadiene-polybutadiene of equal capacity. The process developed by the Institut Français du Petrol has the advantage of being operable with petroleum stream feed stocks of only 10 per cent concentration of isobutylene. The product, isoprene, is obtained in high purity and thus the necessity for capital investment in purification and fractionation equipment is greatly reduced.

The S.N.A.M. process has the advantage of integrating next to a facility for production of phenol by the cumme route, which yields acetone as a by-product. The latter is one of the initial raw materials in this process. In addition, the prospects are good for a drastic reduction in the price of acetylene, the other raw material required in this process. This process is claimed to operate under very mild conditions, the effect of which is to reduce

<sup>&</sup>lt;sup>47</sup> Chemical Engineering, 70: 68 (1963); J. K. Gillham, Science, 139: 494 (1963); and K. Parvin, Plastics Institute Transactions, 31: 132 (1963).

<sup>&</sup>quot; H. Mark and S. Atlas, "Recent Trends in Plastics Research and Development".

he capital investment for the plant, as the majority of the equipment can be constructed from ordinary carbon steel.

In the area of acetylene technologies, it was pointed out that the chemistry involved with acetylene is less complex. However, ethylene commands an advantage because of its lower cost. This situation may change drastically in the near future with the possibility for development of processes using an electric arc plasma system for production of acetylene. In the area of aromatics production, the economic situation which has prevailed in the last few years in the United States in connection with catalytic reforming vs. hydrodealkylation was described because of its potential interest to developing countries planning such facilities.

An important development in the design of ammonia plants is the so-called availability of "packaged ammonia plants" of capacities of 30-60 tons per day of ammonia. These small plants can compete economically with the conventional large-scale plants by utilizing some drastic innovations in design and extensive pre-assembly of plant components.

The liquid phase oxidation process represents a new technology which utilizes mixed feed stocks to produce desirable petrochemical intermediates. By operating at low pressures, some savings in capital investment are effected. The new processes for manufacture of phenol circumvents some of the cumbersome older technology and yields phenol on a lower cost basis in higher yields and at least in one case from an intermediate (cyclohexanol), which is suitable for the production of other petrochemicals also.

The vapor phase oxidation process for production of phthalic anhydride is purported to give very high yields and operate under conditions enabling the plant to be re-started without pre-heating after a shut-down of up to 30 hours. In addition, it is claimed that the catalyst utilized requires little in maintenance costs (in the range of 3-4 per cent of plant investment), and has a guaranteed minimum life of 5 years.

Peracetic acid has been mentioned in conjunction with a new process for production of caprolactam, which avoids the formation of ammonium sulphate as a by-product. The N.O.C. process of the Société Belge de l'Azote for production of vinyl chloride is based on the direct use of diluted pyrolysis gas from naphtha. In this manner, purification and concentration costs for the raw material are minimized.

The production of acrylonitrile from propylene and ammonia is a process which gives a valuable intermediate from inexpensive raw materials. A least a portion of the plant operates at essentially atmospheric pressures (absorber section and all distillation columns). This also has an effect of reducing equipment costs.

A novel catalyst-reclaiming method in the Oxo process has the effect of making this process more economic. In addition, the development of closely related processes which yield tertiary carboxylic acids has the net effect of broadening the versatility of Oxo technology.

It is parhaps useful to state that developing countries should consider in all instances where possible obtaining at least the core of the most advanced technology available. In this manner, the inception of yearly obsolescence can be effectively prevented and competition with already established producers is most likely to be successful. By obtaining the most advanced technology, at least in the core of an industrial development, a developing country can adapt to its specific needs and conditions the process details as most fitting to local requirements.

There is little doubt that science and technology can exert a significant impact on the scope and pace of economic growth in developing countries. One of the crucial questions appears to be how developing countries with a shortage of technological skills can start to utilize the world pool of scientific knowledge and technological achievements. A concomitant problem is recognizing where and when to break the pattern of limited economic activity and attempt to surge ahead with technological innovations.

Although there is no general disagreement on the significant role of science and technology for economic growth in developing countries, opinions vary as to the methodology of implementation. There are those who take the broad front approach that implies aiming at the scientific breakthrough, i.e., the development of new foods, new fuels, and new patterns of social and economic organization.<sup>37</sup> The second approach is that of specifically weking out areas of economic stagnation and developing increments of innovation that may induce productivity and economic growth. This approach takes exception to the premise that scientific and technological data per se are applicable always and everywhere on the face of the earth. It assumes rather that science and technology must work through a process of adaptive innovation, wherein science and technology are modified and adjusted to suit the very special needs and means of developing economies. This factor of local orientation is most imperative in subsistence economies where the barest margins of adjustable variables prevail. Although, in this context, adaptive innovation in fragments, to suit local conditions may appear to be a "boot-strap" operation, it appears to be often an inescapable choice.\*

Irrespective of which approach is adapted by a particular developing country, a few words are in order as to the sources of invention and innovation. Scientific theory and technological practice are interdependent and discovery or invention may emanate from either theoretician or practitioner.<sup>80</sup> In searching for invention or adaptive innovation, neither source can be neglected for results may be readily accessible in either one environment or the other.

Whatever the source of new technology may be, and whatever its nature — invention or adaptive innovation — the absorption and dissemination of scientific knowledge and of technological know-how are phenomena which have a critical impact on economic growth. The

<sup>&</sup>lt;sup>49</sup> R. L. Maiar, Science and Research Development : New Patterns of Living (Cambridge Technologies) Press of Massachusetts Institute of Technology, 1936).

<sup>&</sup>lt;sup>46</sup> J. Barronson, Bullotin of the Atomic Scientist, 16: 151 (1969).

<sup>&</sup>lt;sup>40</sup> James B. Connent, Science and Common Source (Yale University Press, New Haven, 1961).

rate of diffusion of such knowledge and know-how is a direct function of the social and political organization and of the economic environment prevailing.

It is perhaps appropriate to conclude with a few words about the interrelationship between science and technology in developing countries. This subject has been dealt with most lucidly by Caryl P. Haskins in his recent book.<sup>44</sup> He states that one of the most practical reasons why new countries need a science of their own is that technology cannot remain vital and growing without the continuing feedback from a living science. Without an indigenous science, a new country must depend heavily and indefinitely upon constant borrowing for its growing technology not to stagnate. Such permanent dependence upon borrowed technology can be politically as well as technically and economically dangerous for a develop-

<sup>40</sup> C. B. Haskins, The Scientific Revolution and World Politics, Published for the Council on Persign Balations by Harper and Row Publishers, New York, 1964. ing country. For if the management and development of the technologies that it borrows, taxes its resources of understanding and innovation too heavily, technical dependence can easily lead to dependence in the economic and political spheres as well. Furthermore, no one can understand so well the requirements and the new opportunities for technology within one's own land as the people who are actually employed and must live with the consequences. The effective adaptation of technology to local use requires, thus, in the most pragmatic sense both a living and a practical native science. It is no overstatement that, in the long run, a nation can be reckoned truly strong and independent only if it possesses both a vital technology and a vital science in the appropriate balance.

#### ACKNOWLEDGEMENTS

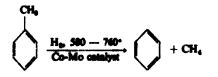
Grateful acknowledgement is given to Chemical Week, Chemical Engineering, and the McGraw-Hill Publishing Company for permission to reproduce figures 2, 3, 4, 5.

## 2. RECENT TRENDS IN PETROCHEMICAL RESEARCH AND DEVELOPMENT

Prepared for the United Nations Centre for Industrial Development by Harold Hart, Prefessor of Chemistry, Michigan State University, United States of America

#### INTRODUCTION

To discuss recent trends in research and development in the petrochemical industry in one lecture is like trying to have a casual conversation with one's wife, over a cup of coffee at breakfast, about the meaning of life. The subject is vast, and the time is short. Some limitations are therefore necessary, and being an organic chemist I first exclude inorganics (ammonia, sulfur) and carbon black, despite their obvious importance (in the United States, over 10 per cent of inorganic tonnage is petrochemically derived). Also excluded are those organic chemicals which might be regarded as primary petrochemicals; that is, major raw materials obtained either by direct recovery from refinery streams (such as lower alkanes, ethylene, propylene, butenes, benzene, toluene, xylenes and hydrogen) or by nonor only partially-specific chemical conversions such as cracking (ethylene, propylene, acetylene) or dehydrogenations and isomerizations (butenes, butadiene, butanes). This is not to minimize the importance of these raw materials, because they are basic to all other petrochemicals. But research on them is largely a matter of engineering rather than organic chemistry. A possible exception is benzene, the demand for which has increased markedly in the last few years. Roughly three-fourths of all benzene produced is consumed in the manufacture of styrene, phenol and cyclobexane, for ultimate use in polystyrene, phenolic resins and nylon respectively. The recent increased demands for these products has resulted in the commercial hydrodealkylation of toluene. Benzene is less prevalent in petroleum aromatics than is toluene by a factor of about four. This is a very good example of research governed by economics, since it could not truly be said to be an aesthetically pleasing reaction for a synthetic organic chemist.



Finally, 1 will omit from the discussion research on the petroshemical and-products themselves, the plastics, resins, surface coatings, synthetic rubbers and fibres, detergents, etc. Rather, attention will be centered on the organic chemicals which are the precursors of these and other end-products; the interesting chemistry of the polymers themselves will be covered (at this conference) by others more competent.

#### FUNDS FOR PETROCHEMICALS RESEARCH

Most of the figures presented apply to the petrochemicals industry in the United States. Although the numbers may be different for other nations with a well developed organic chemicals industry, the trends are probably rather similar. It is evident from the funds spent on research that the chemical industry in general, and the petrochemicals industry in particular depends heavily for its expansion on new ideas from research

 
 TABLE 1. Research funds in the United States of America, 1962

	Company funds for research and development	Funds for basic resourch
	( Millions	of dollars)
Chemicals and allied products .	894	132
Electrical equipment and com- munications	887	90
Motor vehicles and other trans- portation	675	12
Machinery.	633	28
Aircraft and missiles	412	69
Petroleum refining and extrac-	281	47
Professional and scientific instru-		
ments	231	17
Others	817	66

SOURCE: Chem. and Eng. News, march 23, 1964.

and development. In the United States, the chemical industry is first among all industries in spending its own funds for research and development (table 1). its record on basic research is equally good. The apportionment between basic research, applied research and development was approximately 11:37:52, as contrasted with the average of other industries of 4:18:78.

Petrochemicals research accounted last year for somewhat over 29 per cent of the oil industry's total research effort. It seems likely that within the next five years this figure will grow to somewhere between 30 and 40 per cent. In addition, expenditures by other types of chemicals companies can rightfully be considered as partly in the petrochemicals category, since petrochemicals account for over 80 per cent of the tonnage of all organic chemicals produced in the United States. The reason for this generous support of basic and applied research is not altogether altruistic, but becomes apparent when the profit picture is examined. Only 3 per cent of the oil industry's production tonnage is consumed by petrochemicals, yet the total revenue from this small percentage is over 15 per cent of the total.

I have included these figures merely to emphasize for the developing nations whose representatives are gathered here for this conference something which they probably already know but which cannot be omitted from the total picture. The building of plants must also be accompanied by the training of research scientists and the building of research laboratories. Otherwise, the industry cannot be independent and healthy, nor can it grow.

# RECENT RESEARCH AND DEVELOPMENT

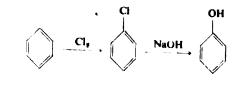
It would be impossible in a brief paper such as this to summarize all recent advances in petrochemical research, for aside from the areas of steroids, proteins, carbohydrates and natural products (and there are some exceptions even here) almost every discovery in organic chemistry has some bearing on the petrochemical industry. In addition, one must include the broadening area of overlap between organic and inorganic chemistry, especially the field of organometallics, as well as research on catalyst materials (alumina, metallic oxides, metal carbonyls, etc.).

In this section, I want to review a few of the major developments in petrochemical research which either have or will shortly be commercialized. The main theme, or driving force behind these developments is the need for multiple routes to a given product, partly to take advantage of different raw materials, partly to get into a large market without having to pay licence fees or royalties, partly to allow for flexibility in case of changes in process economics. An occasional by-product of such research is the discovery of a generally applicable process which may be useful in making new products as well, a notable example being some of the newer oxidation processes which have not only improved the phthalic anhydride or terephthalic acid picture, but have added to the potential of new polyfunctional acids which are or may become commercial.

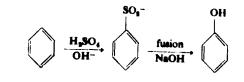
### (a) Phenol

Despite the existence of four major processes for production of phenol, several new processes, which involve new chemistry, have recently been developed. The reasons are clear. The demand is ever-growing; 1964 United States production will be nearly 10 per cent higher than that of 1963, and well over 900 million pounds. All four major processes depend ultimately on benzene as a raw material:

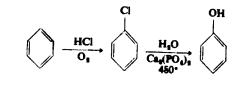
Chlorination



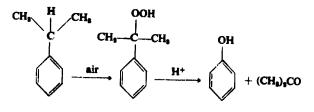
Sulfonation



Raschig oxychlorination



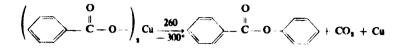
Cumene oxidation



In the last, the cumene is derived from benzene and propylene.

A new route is based on the more plentiful and less expensive toluene, which is first oxidized to benzoic acid by air in molten benzoic acid containing a coppermagnesium benzoate catalyst system. When copper benzoate is heated at 260-300° for several hours it is converted to phenyl benzoate, carbon dioxide and copper. If water is present, for example when the reactants are benzoic acid and copper oxide, one obtains phenol and benzoic acid. The process can be used to efficiently convert two moles of benzoic acid to one mole of phenol and one of benzoic acid by oxygenating the reaction mixture using only catalytic amounts of copper. The

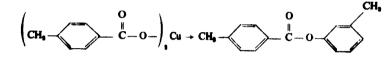
Acrylonitrile production may undergo a very large expansion, should it also become a principal raw material for nylon (adiponitrile).



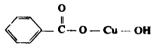
reaction mechanism has not been worked out in detail, but it is known that the hydroxyl group takes a position ortho to the original carboxyl. Thus copper p-toluate affords, in the absence of water, m-cresyl-p-toluate, and m-toluic acid gives a 50:50 mixture of -o and p-cresyl toluates. Interestingly, both 1- and 2- naphthoic acids give 2-naphthol.

### (c) Raw materials for nylons

This has been one of the most active research and development areas in recent years. Some of the numerous routes to conventional 6-6 Nylon, and to new polyamides which have challenged the original Nylon (especially caprolactam, Enant) are shown in figure X. Butadiene



The reaction can be adapted to preparation of salicylic acids. Addition of one mole of copper sulfate to a solution of one mole of benzoic acid and two moles of base gives basic copper benzoate,



or benzene are the "primary" petrochemical sources. Noteworthy recent developments are the conversion of cyclohexane to cyclohexanone oxime with nitrosyl chloride; the reaction is light catalyzed, and probably carried out in the liquid phase in the presence of HCl and NO.

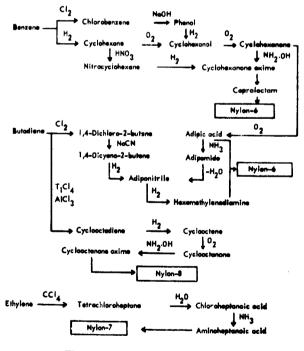
which, when heated dry or in an inert solvent, gives salicylic acid and copper.

Dow now has a plant at Kalama, Washington, for producing phenol based on these reactions.

Another route, which still depends on benzene as raw material, involves air oxidation of cyclohexane to cyclohexano; and cyclohexanone, which are then dehydrogenated; the route presumably is commercial.

# (b) Acrylonitrile

About 500 million pounds of acrylonitrile will be produced in the United States this year 1964, an increase of over 10 per cent from last year 1963. The principle use is as a monomer for acrylic fibers (orlon, acrilan). Addition of HCN to acetylene, using a cuprous chloride catalyst is the source of most acrylonitrile produced today. But newer propylene-based methods are coming to the fore, and ICI has reportedly abandoned the acetylene process in favor of propylene. Methods include various oxidative-aminations (acrolein as an intermediate in certain processes) or oxidation with nitric acids. Acetonitrile and HCN are ammoxidation by-products.





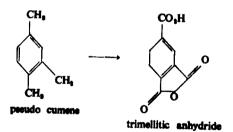
Acrylonitrile may become an important precursor of adiponitrile, through electrolytic reduction. Conversions are very high, and it seems likely that

$$2 CH_1 = CH - CN \xrightarrow{(H)}{2} NC \cdot CH_1 CH_1 CH_1 CH_1 \cdot CN$$

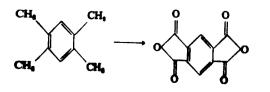
the process, developed by Monsanto, will become commercial. Nylon-7 (Enant) is reported in production in the USSR. The initial step is the telomerization of ethylene and carbon tetrachloride to 1,1,1,7-tetrachloroheptane which is converted, via 7- aminoheptanoic acid to a polyamide. Nylon-8 can be made as described in figure X, the first step being a unique butadiene dimerization.

### (d) Oxidation of alkylbenzenes

Because of the tremendous growth in the use of polyester fibres (Dacron, Terylene, Lavsan), a large research effort has been expended in recent years on improved techniques for oxidizing alkylbenzenes to the corresponding carboxylic acids. The conventional oxidant for p-xylene has been nitric acid, but there are problems with completing the oxidation and with high raw material cost. A new process, used now not only for the three phthalic acids, but for benzoic acid as well, involves a liquid phase air oxidation using acetic acid as the solvent, and a manganese or cobalt catalyst containing added bromide. Typical temperatures are 190-200° with corresponding pressure to maintain the liquid phase. The reactions are clean and yield is high, but solvent must be recovered for suitable economics. The reaction, which proceeds by a free radical mechanism, is general for a variety of alkylaromatics, and it is likely that a number of new acids will be available commercially as a result of this process.



Trimellitic anhydride is now produced from pseudo cumene by this method; being both an acid and an anhydride, it has many interesting chemical properties which are finding commercial application. Pyromellitic anhydride, a bis-anhydride prepared by oxidizing durene, also promises to see expanded use.

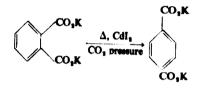


California Research Corporation has described the use of sulfur and water as oxidant for toluene and xylenes. The reaction is driven to completion by adding

$$\bigcirc - CH_{a} + 3S + 2H_{4}O + \bigcirc - CO_{4}H - 3H_{4}S$$

sulfur dioxide to react with the hydrogen sulfide, forming more sulfur for the oxidation step.

A process which avoids p-xylene as the raw material for terephthalic acid involves the cadmium-catalyzed isomerization of potassium phthalate. The reaction is carried out in the presence of  $CO_8$  at 50-100 atmospheres and 380-420°.

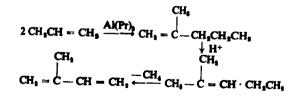


The potassium terephthalate can be converted directly to the dimethyl ester for use in fiber synthesis.

It is possible that toluene may become a raw material for terephthalic acid, via carboxylation, chloromethylation or reaction with carbamyl chloride; these processes are not yet commercial.

### (c) Isoprene

Of the various synthetic rubbers now on the market, the most common by far is styrene-butadiene copolymer. It seems likely that most future growth in synthetic rubber will come from new classes, of which ethylenepropylene rubber and polyisoprene stand out. The limitation on the latter is availability of raw material, and several new processes are being developed for isoprene synthesis. Dehydrogenation of isopentene or isopentane gives a mixture of products. A newer process involves dimerization of propylene using an alkylaluminum catalyst, isomerization to the 2-olefin and pyrolysis to obtain the five-carbon diene and methane.



A possible future route is from isobutylene and formaldehyde (Prins-type reaction). The suitable carbon skeleton might also be constructed from acetone and acetylene, or methyl ethyl ketone and formaldehyde.

I have reviewed above very briefly five of the major synthetic developments in petrochemicals during the last few years. Obviously, there are many others, which space and time to not permit me to review. These serve only as examples of the claim made above that the petrochemicals industry must depend for its growth on an active and vigorous supporting research effort.

Perhaps attention should be called here to the very large number of specialty chemicals available from petroleum sources. These are chemicals manufactured on what for the petrochemicals industry is a very small scale (perhaps one to ten million pounds per year). These are substances with special uses, additives, possibly starting materials for phamaceuticals, perfumes, insecticides, pesticides, fungicides, etc. Obviously these are extremely important, and the profit is rather high relative to monomers for plastics, fibers and rubber. But the variety of organic structures is so great that a systematic discussion of the research which has led to their development would be impossible here. Some of these substances may find good markets in certain of the developing nations, and may be profitable for them to manufacture. But it seems unlikely that new petrochemical plants, or perhaps more accurately a new petrochemical industry could be based on such small volume production. For this reason, I have omitted them from the present discussion.

# NEW FRONTIERS FOR FUTURE PETROCHEMICALS

In the following section of this paper, I should like to call attention very briefly to what I consider some of the major recent developments in organic chemical research which are now affecting petrochemicals research, or which are likely to do so in the future. Once again, it has been necessary to omit more than it is possible to include, but those which are mentioned may be a reminder of others, to those who read this paper.

# (a) Hydroboration

The reaction of boron hydrides with olefins is known as hydroboration. The scope of the reaction was first recognized in 1956, and in 1962 results were

$$\mathbf{C} = \mathbf{C} + \mathbf{H} - \mathbf{B} \mathbf{C} + \mathbf{C} - \mathbf{C} - \mathbf{B} \mathbf{C}$$

summarized in a book by H. C. Brown, the principal investigator in this field. The reaction can be used to isomerize internal to terminal olefins, to convert olefins to terminal alcohols by a process which involves, in effect, anti-Markownikoff addition of water to the double bond (thus supplementing the ordinary acidcatalyzed hydration of olefins), and to transform acetylenes to cis-olefins or to carbonyl compounds.

$$3(CH_1CH = CH_1) + B_1H_1 \longrightarrow 2(CH_1CH_1CH_1)_B$$

$$(CH_{8}CH_{9}CH_{9}CH_{9}B + 3H_{9}O_{9} \xrightarrow{OH^{-}}{25 - 30^{\circ}} 3 CH_{9}CH_{9}CH_{9}OH + B(OH)$$

$$C_{6}H_{9}C = CH + R_{9}BH \longrightarrow C_{6}H_{9}CH = CHBR_{9}$$

$$\downarrow H_{9}O_{9}$$

$$C_{6}H_{9} \cdot CH_{9} \cdot CHO$$
(88 % overall)

Cyclopropanes can be prepared from the allyl chloride adduct in quantitative yield.

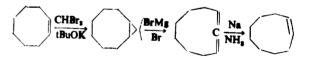
$$HO \rightarrow B - CH_{1}CH_{2}CH_{3}CH \rightarrow HO - B + CH_{1} - CH_{1} + CH_{2} + CH_{2} + CH_{3$$

Although the reagent is still expensive, and the reactions are used primarily in laboratory synthetic work (analogous perhaps, to the Grignard reagent) it is not unlikely that suitable modifications, perhaps in the form of developing catalytic processes in which the organoborane is a transient intermediate, will lead to industrial applications.

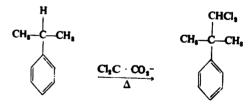
Borohydride reduction of various metallic ions (nickel, platinum, rhenium) has led to new hydrogenation catalysts with varying degrees of specificity which may also find petrochemical application.

### (b) Carbenes

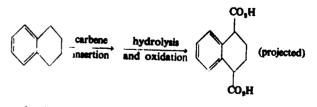
Certainly one of the great developments in organic chemistry during the last ten years has been in the field of divalent carbon species — methods for their generation are now numerous, and their reactions are becoming well understood. Depending on the method of generation, they may be produced in the singlet or triplet state (which behave differently chemically) and their reactivity can be modified over a wide range by association with metal ions. Cyclopropanes produced from olefins can now be used in many new reactions, as for example, the Doering allene synthesis (specific example shown by P. D. Gardner). Insertion reactions are adaptable to many new functional group syntheses. Application to



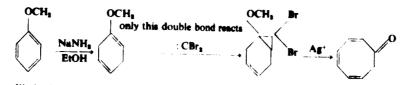
difunctional hydrocarbons could lead to interesting new monomers difficult to



synthesize in other ways. Advantage can be taken of special functional group



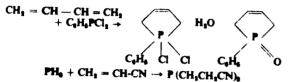
activation, as in the selective reaction of the methoxylated double bond in the Birch reduction product of



anisole. It would seem likely that carbones (methylenes) will ultimately find their way into commercial petrochemicals.

# (c) Use of elements other than C,H,O,N,S,

In this brief paper we can do no more than to call attention to the intimate overlap inorganic and organic chemistry by mentioning a few of the elements now common in organic compounds as, for example, F, especially in fluorocarbons, Si, in silicones and P in organo phosphorus compounds. Consider, for example, the intriguing synthetic possibilities of the following reactions:



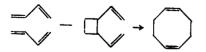
B (See hydroboration, above; new B-N containing aromatic systems, such as



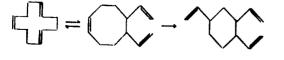
open up new vistas in unusual polymers, etc.) Fe (metallocene chemistry; it seems likely that many of the answers to metal catalysis of organic reactions will come from fundamental studies of metal-organic complexes, especially those with olefins and aromatics) and many others. Some of these materials are now produced commercially; others are sure to follow, and the area seems like a profitable one for future petrochemical development.

# (d) Valence tautomerism

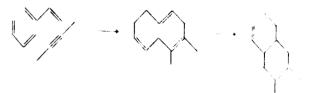
A good deal of interest has been aroused recently in so-called no-mechanism rearrangements, or valence tautomerism. Much of the work concerns olefins, and has led to new syntheses and new ring systems which may become readily accessible from petrochemical raw materials. One is reminded, for example, of the dimerization of butadiene to 1,5-cyclooctadiene, now



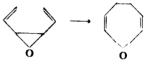
available commercially, or of the interconversions of the trimer, cyclododecatriene. Through the combination of transition metal-  $\pi$  - complexes



chemistry and thermal rearrangements, many new olefinic raw materials are becoming available. It seems likely that the next five years will see commercialization of some of these interesting olefins. Acetylenes may also be



used, as in the reaction sequence. Heterocyclic compounds also undergo such reactions.



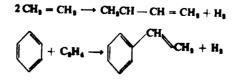
New monomers can easily be envisioned from such materials, as well as, of course, specialty chemicals. The raw materials are relatively low priced, and the processes could be developed provided uses for the end products were at hand.

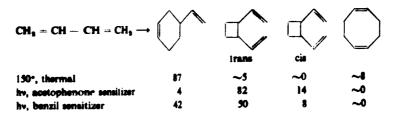
# (c) New energy sources

All of the reactions discussed thus far are conventional in the sense that the activation energy for reaction is provided by thermal energy (except for mentioned electrochemical reactions). But new energy sources are currently being explored for their possible synthetic utility. An example is the field of fissiochemistry or the use of nuclear fission energy to make chemicals. In most cases the reactive intermediates are radicals (sometimes radical-ions) produced with high energy. Among reactions which are being studied are

$$\begin{array}{rcl} 2\mathrm{NH}_{\bullet} & \longrightarrow \mathrm{NH}_{\bullet} - \mathrm{NH}_{\bullet} + \mathrm{H}_{\bullet} \\ 2\mathrm{CO}_{\bullet} & \longrightarrow 2\mathrm{CO} + \mathrm{O}_{\bullet} \\ 2\mathrm{CH}_{\bullet}\mathrm{OH} & \longrightarrow \mathrm{MOCH}_{\bullet}\mathrm{CH}_{\bullet}\mathrm{OH} + \mathrm{H}_{\bullet} \\ 2\mathrm{H}_{\bullet}\mathrm{O} & \longrightarrow \mathrm{H}_{\bullet}\mathrm{O}_{\bullet} + \mathrm{H}_{\bullet} \end{array}$$

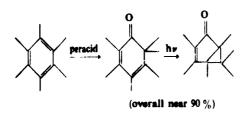
as well as nitrogen fixation, and the formation of ozone from oxygen. One can envision possible applications, now in the realm of fantasy, which might be important to the petrochemical industry:





Our understanding of the interaction of light with organic molecules is becoming clearer as a result of current research. Although strictly not a new energy source, the commercial use of light to carry out large scale, otherwise difficult syntheses, seems inevitable and can be classed as new. As an example of the dramatic effect of light catalysis (and of the use of sensitizers) on a recation course, one may consider the following transformations of butadiene.

The following example from our own laboratory illustrates possible applications to aromatic hydrocarbons.



Concentrated energy dosages, as from lasers, may ultimately have applications to petrochemicals.

### **CONCLUSIONS**

Even though I have barely touched, in this paper, on the tremendous scope of research in the petrochemical industry, it should be clear from the examples given that, perhaps to an extent greater than in most industries, progress and rapid advance on a technological level can only be the result of imaginative, long range basic research, ultimately teamed up with practical development work. The basic research must be given free rein, for one cannot predict from which river of research new products will flow. This will be true as the petrochemical industry becomes important in the developing nations just as it has been elsewhere until now.

It is impossible for me to be so presumptuous as to recommend that this area of research, or that development problem should be undertaken by a particular nation which is developing a petrochemical industry. Each country will have to decide these problems after assessing its needs, raw materials, potential market etc. But included in any of these plans should be the thought that a strong supporting programme of training, research and development will be necessary if the industry is to flourish.

# 3. RECENT TRENDS OF PETROCHEMISTRY IN THE MACROMOLECULAR FIELD

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### INTRODUCTION

In the age we live in, crude oil has become a vital lymph; without it, the modern way of life on Earth would be paralyzed in a very short time.

The importance of crude oil in the various fields of modern life is so great that not only technicians, but politicians and economists all over the world focus their attention on it.

Though less obviously, crude oil has acquired great importance also as a raw material for several chemical syntheses. This has originated a very important branch of the present industrial chemistry: i.e. petrochemistry. In fact from crude oil, or better from its products and by-products, it is possible to obtain by chemical reactions substances that are useful in different fields of application.

The products that can be obtained from crude oil by chemical reactions are numberless; thousands of pages would be necessary to describe this topic thoroughly. In this paper we can only point out the importance of crude oil as a raw material for the production of high polymers, that is of substances fit to obtain plastic materials, textile fibres and synthetic rubbers.

# RAW MATERIALS AND INTERMEDIATES

In the refineries crude oil is subjected to a great number of treatments, in order to obtain higher yields in valuable products having greater demand on the market. Topping, cracking and reforming processes, the distillation under vacuum of lubricant oils, alkylation and polymerization processes, are all adressed to obtain the highest amount of valuable products from crude oil, i.e., gasoline, fuel oil, lubricants of various viscosities and related products.

This operation cycle, however, yields along with the desired fractions, more or less high amounts of products, which have less demand on the market; moreover some of the operations mentioned above (e.g. cracking) lead to the production of volatile hydrocarbons rich in unsaturated compounds, which cannot be sold as fuels owing to both their high volatility and to their degree of unsaturation. Unsaturated hydrocarbons contained in these volatile fractions mostly consist of olefins, diolefins containing up to five carbon atoms; after purification their compounds can be used for the production of high polymers.

Also the distillate fractions which are less in demand can be subjected to cracking under suitable conditions so as to give high yields of volatile hydrocarbons rich in the above-mentioned unsaturated compounds.

For instance, in Europe the insatiable consumer demands for fuel-oil, gasoline, lubricants, etc. make it necessary to add refinery capacity at a growing rate; this situation leaves at disposal big quantity of naphtha, which is not in high demand. Thus naptha has become the preferred material as feedstock for the steam cracking in the production of olefins in most countries in Europe.

Thus, from the refinery or from auxiliary plants, it is possible to obtain a considerable amount of low-molecular-weight unsaturated hydrocarbons that can be used in chemical syntheses or directly for the production of high polymers.

In table I we list the olefins and diolefins present in hydrocarbon fractions having up to 5 Carbon atoms, as well as their boiling temperatures. As we shall see, from these compounds it is possible to obtain a considerable amount of high polymers, which are interesting for the production of plastics, synthetic rubbers and fibres. Obviously the refinery or cracking gases contain, along with olefins and diolefins, other hydrocarbons such as the corresponding saturated compounds (ethane, propane, butane, isobutane, etc.), or unsaturated compounds of other hydrocarbon-hydrocarbon gases (CO, H<sub>8</sub>, etc.).

# TABLE 1. UNSATURATED HYDROCARBONS UP TO $C_8$ praction obtained in steam cracking of Naphta

										_						Boling poin °C
Ethylene																- 103.9
Propylene									•	·	•	•	•	•	•	- 47
Butene-1				Ċ		·	•	•	•	•	•	•	•	•	·	
Butene 2 cie	•	•	•	•	•	•	•	•	•	•	•	•	•	٠	•	5
Butene-2 cis.	•	•	٠	•	•	·	٠	٠	٠	٠	٠	•	•	•	•	1
Butene-2 trans.	٠	٠	•	•	•			•								2.5
sobutene																6
Butadione												÷	·	·	•	-
-methyl-buten	<b>1</b>	-	•	·	·	•	·	•	•	•	·	•	•	•	·	- 3
mathal house		•	•	•	•	•	•	•	٠	٠	٠	٠	٠	٠	·	31
-methyl-butene	-2	•	٠	٠	٠	٠		•	•	•	•	•				38.5
soprene	•	•	•	•												34
iperviene												·			•	43
>volopentadien			ĺ.	Ĩ			•	•	•	•	•	•	•	•	•	
		•	•	•	•	•	•	•	•	٠	•	٠	٠	٠	•	42.5

A lot of other unsaturated hydrosarbons are also present --- in seall percentage.

Therefore, in order to employ olefins or diolefins in chemical syntheses or in polymerization, it is necessary to perform several separation, fractionation and purification processes of the various hydrocarbons. These separation processes are usually carried out by low temperature distillations in several fractionation columns. thus high-purity olefins or diolefins are obtained.

The polymerization of olefins and diolefins generally requires, for these monomers, a high degree of purity; in fact, high concentrations in inert compounds must be avoided in order to have a high concentration of the monomers in the polymerization and to have recycle of monomers without raising the concentrations of inerts; above all the presence of compounds that act as poison for the polymerization must be reduced as much as possible. For this reason, the fractionation of ethylene, of propylene and of other monomers is particularly controlied by accurate analyses; table II reports the comprisition of ethylene and of propylene suitable for the polymerization; the type and highest amount of negligible impurities are indicated.

TABLE II. ANALYSIS OF ETHYLENE AND	PROPYLENE SUITABLE FOR THE
POLYMERIZA	LION

Etyhlene.	Min. 99.8 per cent	Max. 50 p.p.m.
Propylene	Max 500 p.p.m.	Min. 99.8 per cent
Oxygen .	Max. 20 p.p.m.	Max. 20 p.p.m.
Hydrogen	Max. 100 p.p.m.	Max. 100 p.p.m.
Carbon monoxide		Max. 5 p.p.m.
Acetylene	Max. 50 p.p.m.	
Ethane		
Carbon oxysulphide.		Max. 5 p.p.m.
Total sulphur		Max. 10 p.p.m.
Carbon dioxide.		Max. 10 p.p.m.
Allene		Max. 5 p.p.m.
Methyl acetylene		Max. 2 p.p.m.
Water.		Max. 10 p.p.m.

### HIGH POLYMERS OBTAINABLE FROM CRUDE OIL

A considerable production of high polymers deriving from monomers obtained from crude-oil started a long time ago. In fact various unsaturated polymerizable compounds can be easily obtained by relatively simple chemical reactions from the olefins and diolefins mentioned above. As an example, let us consider ethylene. From is, by addition of chlorine and subsequent dehydrochlorination, vinyl chlor de is obtained, which can be polymerized to polymers and copolymers with excellent properties; by the addition of ethylene to benzene and subsequent dehydrogenation, it is possible to obtain styrene, which is an important monomer for obtaining different plastics (pure and modified polystyrenes, ABS alloys and copolymers) and synthetic rubbers (SBR rubber). The direct oxidation of ethylene yields ethylene oxide, which can be used for different purposes; one of the most important is the hydration to ethylene

glycol; this last is employed for the synthesis of polyethylenterephthalate, used for the production of polyester films and fibres.

These few examples concerning ethylene, which however are analogous for other olefins, give an idea of the versatility of these compounds and of the great number of polymeric materials that can be obtained. This versatility explains the great demand of ethylene and of other olefins all over the world. As an example, with reference to the European countries and in particular to the European Economic Community (EEC), the present total capacity of ethylene is of about 1,4 million metric tons, while that of propylene is of about 1 million metric tons. The estimates based on known plans allow to foresee for 1966-67 a capacity of 2,8 million metric tons for ethylene and of 1,8 million metric tons of propylene.

Taking Italy as an example, the olefin picture is as follows:

			Ртегени сарасну	1965-66 capacity
Ethylene . Propylene .			360,000 metr. tons 220,000 metr. tons	500,000 metr. tons 315,000 metr. ions

This river of olefins will flow into a complex web of petrochemical plants that will transform this raw material into an impressive list of products.

However, the examples mentioned before involve a previous chemical transformation of unsaturated hydrocarbons into other bifunctional polymerization compounds; these chemical reactions concern the field of petrochemistry.

A fairly wide and important field of polymeric materials comprises hydrocarbon polymers and copolymers that can be directly obtained by polymerization of one or more olefins and diolefins. This specific field will be dealt with in this lecture.

### HYDROCARBON POLYMERS AND COPOLYMERS

A considerable production of these materials, making a convenient use of raw materials deriving from crude oil, started a long time ago. This production has considerably increased in the last few years, both as regards type and quality of polymers, thanks to the new anionic coordinated polymerization processes. Until a short time ago, the production of high hydrocarbon polymers was limited to polyethylene, polyisobutylene, to the isobutene-isoprene copolymers (butyl rubber) and to the butadiene-styrene copolymers (SBR rubber).

Let us consider the present stage of these polymers and copolymers, to evaluate better the future prospects of the new polymers.

### POLYETHYLENE

At present, ethylene can be polymerized to high polymers by different processes; thus it is possible to obtain numberless types of polyethylenes, which differ in their degree of crystallinity (usually expressed with density measurement), in their average molecular weight (expressed by the measure of the melt index), in the distribution of the molecular weights. The physical and chemical properties of polyethylene vary as a function of these three parameters, sometimes very markedly.

The wide field of applications of this polymer (films, blown containers, coatings, moulded articles, pipes, wire and cable) are mainly due to its flexibility (which is kept also at low temperature) to its impact strength, to its impermeability to water, to its good electric properties also at low frequency and to its good chemical resistance.

The world consumption of polyethylene has undergone a fantastic increase in the last few years; at present, the world production is of about 2 millions tons/year and, as foreseen, it will increase steadily in future years.

In table III, we report some figures of production of polyethylene, referring to Italy, EEC (comprising of course Italy) and the United States of America for different years (the values of 1966 are estimates).

TABLE	111.	PRODUCTION	of	POLYETHYLENE *
		(Tons/ye	ar)	

	USA	EBC	Italy
1955	182,000	20,000	5,000
1963	1,010,000	370,000	91,000
1966	1,250,000	565,000	110,000

\* Totalling high and low density types.

The importance of the polyethylene production can be easily pointed out by the comparison with the data concerned with the production of olefins; polyethylene alone in EEC represents about 30 per cent of the total production of ethylene.

# POLYISOBUTENE-BUTYL RUBBER

The polymerization of isobutene is carried out with the aid of cationic-type catalysts at low temperature; the other conditions being the same, the lower the polymerization temperature is the higher the molecular weight. Polyisobutene is an amorphous rubber-like polymer, having good electric properties and chemical resistance; it is used for the production of coatings, of adhesives mixed with other polymers in order to improve some properties, in addition to lubricant oils to improve their viscosity index.

The copolymers of isobutene with small amounts of isoprene, i.e., butyl rubber, are even more important than polyisobutene. This rubber can be vulcanised by reaction with vulcanizing agents of the residual double bonds of isoprene; it shows a high impermeability to gases, and high aging resistance properties; it is mainly used for the production of inner tubes, cables or technical articles, which require a good aging resistance. This rubber, due to its scanty dynamic properties cannot be widely used for the production of tyres, even if tyres made of butyl rubber have some interesting properties, e.g. good adherence to wet roads.

# BUTADIENE-STYRENE COPOLYMERS

These copolymers, which presently represent the synthetic rubbers of greater production, were largely prepared for the first time, on an industrial scale, during World War II, to make up for the scarce availability of natural rubber. After the War, they held out against the competition of natural rubber, both because of the continuous improvements made on these clastomers and because the production conditions, since the starting monomers are derived from petroleum, were advantageous from the economical point of view. The properties of butadiene-styrene rubbers, even if less good than those of natural rubber from a dynamic and mechanical point of view, are on the whole sufficiently good and can be used for the production of tyres. The economic advantage of these rubbers is further increased by adding to them considerable amounts of hydrocarbon oils of low price. The field of applications of butadiene-styrene rubbers is fairly wide and favoured not only by the properties of these elastomers, but also by the advantage of constant quality and price.

The production of these synthetic rubbers is already considerable: in the United States, for instance, it was of 1,250,000 tors/ycar in 1963. Forecasts on these rubbers are rather uncertain, since other synthetic rubbers, which we will deal with later, are aiready on the market, having either better qualities or more favourable economic prospects. In table IV we report both values or estimates for the countries mentioned above:

TABLE IV. PRODUCTION OF STYRENE-BUTADIENE RUBBER

USA	EEC	Italy
803.000	10.000	
		86.000
	400,000	86,000 100,000
	803,000 1,000,000	803,000 10,000 1,000,000 350,000

# NEW OLEFIN POLYMERS AND COPOLYMERS

As we have seen, some olefins and diolefins could already be used advantageously for the production of considerable amounts of hydrocarbon polymers and copolymers; however, that situation did not allow the complete use of other olefins, which are also available in big amounts.

In the steam cracking of naphtha, for each pound of ethylene, 0.5-1 pound of propylene and about 0.4-0.5 pounds of  $C_4$  olefins and diolefins are produced, depending on the cracking conditions. The use of at least some of these olefins (e.g. propylene) for the production of polymers and copolymers might constitute a useful outlet under favourable economic conditions.

The new anionic co-ordinated polymerization processes discovered ten years ago at the Polytechnic Institute of Milan, by developing the organometallic catalysts proposed by K. Ziegler for the polymerization of ethylene, made it possible to obtain several new polymers and copolymers of olefins and diolefins endowed with excellent chemical and physical properties. By these new processes it was possible to make use of propylene for the production of high polymers; this monomer in fact had never been exploited before for this purpose and was mostly left unemployed. In fact, all efforts made in order to obtain high polymers from propylene, had always led to the synthesis of oily products containing, in some cases, small percentages of higher molecular weight fractions; these products did not show any practical interest.

The new polymerization processes have made it possible to use all the monomers contained in the light fractions deriving from the crude oil processing. Propylene, butene-1, butene-2, butadiene, isoprene, etc. can be polymerized to different polymers that can be suitably employed for the production of plastics, fibres, films and synthetic rubbers. This is an advantage for the new plants, which can be easily planned to vary their production according to the products demand.

Now we wish to describe in more detail the various new polymers and their specific fields of application.

### POLYPROPYLENE

The new stereospecific polymerization processes have made it possible to obtain from propylene several polymers differing in physical properties, though having the same chemical composition. This different behaviour is caused by the different steric structure shown by these polymers; in fact two types of monomeric units of opposite steric configuration can be originated from propylene. The different polymers of propylene show a different arrangement of the monomeric units constituting them.

Isotactic polypropylene has a high regularity of chemical and steric structure; in fact, the tertiary carbon atoms present along the chain have, at least for long portions, the same steric configuration.

Atactic polypropylene, instead, possesses tertiary carbon atoms of opposite steric configuration, which follow one another in an irregular manner along the polymer chain. Besides these two polymers, it is possible to obtain by synthesis either syndiotactic polypropylene (in which the tertiary carbon atoms show opposite steric configurations that alternate regularly along the chain) or stereoblock polypropylene (in which sequences of tertiary carbon atoms having the same steric configuration alternate with others having different steric configuration).

The differences in the steric structure exert an influence on the physical properties of the various polypropylenes; isotactic polypropylene, thanks to its regularity of structure, is a crystalline polymer having high melting temperature and excellent mechanical properties.

The atactic polymer, instead, is an amorphous rubberlike product, which can be transformed into a cured elastomer by suitable crosslinking procedures.

The commercial production of polypropylene is oriented toward the preparation of polymers having a high content in isotactic polymer (generally higher than 90 per cent). In fact, this material has excellent mechanical and thermal properties. In table V the properties of polypropylene are reported.

TABLE V. PHYSICAL PROPERTIES OF POLYPROPYLENE HAVING A HIGH ISOTACTIC CONTENT

Density .	s/cm <sup>s</sup>	0.90-0.91
Yield point		300-360
Tensile strength		300-400
Elongation at break	-	500-700
Tensile modulus of elasticity		12,000-18,000
Stiffness		9,000-15,000
Rockwell hardness.		90-95
Impact strength		> 30
Water absorption		pratically nil
Melting point		175
Softening point	•C	85-105
Vical (5 kg load)		•5~105
Dielectric constant		2-2.i
Loss factor.	. —	2-3 × 10-4
Dielectric strength	kV/mm	30-35

The high melting temperature of isotactic polypropylene allows its use also at those high temperatures at which most of the other hydrocarbon thermoplastic materials undergo a marked deformation. Moreover, this polymer can be easily processed with the machinery usually adopted for thermoplastic materials (extrusion, injection moulding, thermoforming, etc.). The excellent physical-chemical properties and the high surface glass make polypropylene suitable for numberless applications. In every field, this new plastic material has drawn the attention of producers and consumers. It can successfully substitute traditional natural products or other plastics that are not specifically suitable to the purpose.

An application of isotactic polypropylene of particular interest is its transformation into *textile fibres*. The production of these textile fibres is carried out by melt spinning of the polymer followed by stretching and heat treatments.

Polypropylene fibres are already produced on a commercial scale, as continuous filaments and as staplefibre (wool or cotton type); they possess excellent mechanical properties (table  $\forall$ I), abrasion resistance, thermal non-conductivity and crease resistance.

Since these fibres have a low specific gravity (0.91 g/cm<sup>3</sup>) it is possible to obtain, at equal weight and titer, much bigger surfaces of fabric than with all other and synthetic fibres.

# TABLE VI. PROPERTIES OF POLYPROPYLENE FIRES

Tensile strength					g/den	5-8
Elongation at break.					1	20-25
Modulus of elasticity			,		g/den	50-65
Wet tenacity					g/den	5-8
Knot tenacity				,		85
Plax life					D/PEVS.	200.000
Shrinkage (water 100°C)					•4	0
Resistance to Irichloroet	nyk	oni	١.			nood

The production of textile fibres from polypropylene will have a greater importance after improving their resistance to the degradation agents (in particular their resistance to light) and after making their dyeing possible by the cheap dyeing methods usually adopted for other textile fibres. Different methods have been proposed for this purpose and already give positive results. However, it is still too early to foresee which methods will gain favour of the textile industry.

Thus, it is now possible to obtain, directly by polymerization of propylene, polymers that can be used in the production of plastics, films and textile fibres. The production of polypropylene has already asserted itself in Italy, Japan, the United States and in other countries. As an example, we report here the consumption registered in the United States last year (table VII).

# TABLE VII. CONSUMPTION OF POLYPROPYLENE IN THE UNITED STATES (1963)

											 	 	Million Ib.
Moulded article	<b>.</b> .												70
Film and sheet.													26
Monofilament .													22
Fibres.	•	•	•	•	•	•	•	•	•	•	•	•	13
Miscellaneous *													25

\* Miscellaneous includes blow moulding, pipe, wire costing, stc.

Considering that polypropylene was discovered a fairly short time ago, the present production is already very high and it appears that the future success of polypropylene will be at least equal to that of polyethylene.

In fact, it must be borne in mind that isotactic polypropylene, besides being employed in similar fields of application as polyethylene (moulding, film, etc.), can be widely used for the production of fibres.

### POLYBUTENB-1

The  $C_4$  fraction contains butene-1, butene-2 (both cis and trans), isobutene as olefins, as well as more or less considerable amounts of butadiene-1,3 and of saturated hydrocarbons.

After separation of isobutene, this fraction can be used for the production of high-purity butadiene suitable to obtain different synthetic rubbers. However, butene-I can also be polymerized to crystalline isotactic polybutene-I by the new stereospecific polymerization processes. The polymerization can be carried out without separating butene-I from butene-2, which is practically inert toward the polymerization in the conditions adopted in this case.

Isotactic polybutene-1 is a crystalline polymer having physical and mechanical properties similar to those of low-density polyethylene (table VIII). In practice, it is produced by the same apparatus used for the production of polypropylene. Polybutene films have a high tear resistance, while pipes of this polymer are flexible and can carry water at 80°C without being considerably deformed.

TABLE VIII. PHYSICAL PROPERTIES OF POLYBUTENE-I WITH A HIGH MOTACTIC POLYMER CONTENT

Density							g/cmª	0.89-0.90
fonsile strength.							kg/cm <sup>2</sup>	350-400
Elongation al break.							- %	300-400
Stiffness							kg/cm <sup>s</sup>	1,000-2,000
Hardness							Shore D	40-60
Melting point							Ŷ	130-135
Softening point Vicat	t (1	ka	lo	t)			ċ	80-90
Dielectric constant	÷.							2-2.1
Dielectric strength					÷		kV/mm	30-32

### POLYOLEFIN ELASTOMERS

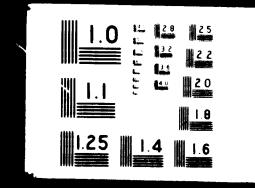
It was already pointed out that from propylene, under suitable polymerization conditions, it is possible to obtain atactic polypropylene, a rubber-like product that can be transformed into a cured elastomer. The dynamic properties of this rubber, however, are poor; therefore its use is limited. For this reason, studies were carried out to find the most suitable systems that might yield elastomers based on olefins endowed with good dynamic properties.

This aim was achieved by the synthesis of elastomers based on ethylene and propylene; they contain, in their macromolecule, the two monomeric units distributed at random. Thus the copolymers containing more than 35 mole-per cent of propylene are amorphous and have a rubber-like behaviour. The sequences of methylenic groups, due to the ethylene units present in the macromolecular chains, make the chain flexible, so that the dynamic properties of these synthetic rubbers are fairly good.

These elastomers can contain in their chain not only ethylene and propyiene, but also small amounts of other hydrocarbon monomers, which. after polymerization, still contain a double bond, useful for the vulcanization with sulphur and accelerators. On the contrary, in the case of completely saturated copolymers, the vulcanimation can be carried out with the use of organic peroxides. In any case, either as copolymers or as ter-

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polymers, these elastomers have mechanical and dynamic properties that are equal to or even better than those of the previously known synthetic rubbers, an exceptional resistance to ageing, to high temperatures, and to degradation agents. Their resistance to ozone is far higher than that of the most used synthetic rubbers. In the preparation of terpolymers, use is made of ethylene and propylene, with different types of third hydrocarbon monomers containing more than one double bond, which too are derived from petroleum. Among all those proposed, we wish to remind dicyclopentadiene (obtained by spontaneous dimerization of cyclopentadiene), 1,5-cyclooctadiene (by catalytic dimerization of butadiene), methylenenorbornene (by addition of allene to cyclopentadiene), divinylcyclobutane, hexadiene-1,4, 2-methylpentadiene, etc.

Elastomers based on ethylene and propylene are already produced on a commercial scale in Italy and in the United States.

The interest aroused by these products is not only due to their physical and chemical properties, but also to economic factors. In fact, these rubbers have a low density (lower cost with the same volume), accept considerable amounts of low-cost oil and fillers, and are produced from raw materials (ethylene and propylene) available or obtainable in great amounts and at low price. All these factors permit the forecast that the demand of these new elastomers will increase rapidly: for instance, the U.S. consumption in 1964 will be about 25 million lb and for 1970 is foreseen to reach about 1 billion pound.

### DIOLEFIN POLYMERS

### Cis-1,4 polybutadiene

The polymerization of butadiene has long been known but in general the polymerization methods known until 10 years ago gave irregular amorphous polymers with rubber-like properties, which did not provide much practical interest. This was due to the fact that in the polymerization of butadiene, it is possible to have different types of monomeric units.

However, by stereospecific polymerization, it has been possible to prepare butadiene polymers having a high structure regularity. The four stereoisomers of polybutadiene have all been obtained with a high degree of steric purity. The physical properties of these polybutadienes differ considerably and this must be attributed to the different type of steric order. Of the four types of trans-1,4 polybutadiene, isotactic-1,2 and syndictactic-1,2 polybutadienes are crystalline polymers with elastomeric properties at room temperature. Polybutadiene having a high cis-1,4 units content, on the contrary, melts below room temperature and therefore shows elastomeric properties.

The structure of this polymer is fairly similar to that shown by natural rubber; its chain has a good flexibility. This is why cis-1,4 polybutadiene with high steric purity (> 96 per cent) shows excellent dynamic properties (equal to or higher than those of natural rubber), which, along with its high abrasion resistance, makes it very suitable, especially if mixed with natural or synthetic rubbers, for the production of those articles (tyres) that must undergo deformation repeatedly.

The production of cis-1,4 polybutadiene, on a commercial scale, started some years ago in several countries and is increasing. By the continuous improvement of the polymerization plants, the production of this elastomer is economically advantageous; thus its price is only a little higher than that of the synthetic rubbers of wider use, and lower than that of natural rubber.

Thus the use of this polymer mixed with natural rubber or with butadiene-styrene rubbers is very advantageous from the qualitative point of view, and also the price picture looks very favourable.

### Cis-1,4 polyisoprene

Natural rubber consists of polyisoprene having a high cis-1,4 unit content (> 97 per cent). Several efforts were made in the past, but without success, to produce natural rubber by polymerization of isoprene, which is present in the  $C_s$  fraction of crude oil products or can be purposely produced from that fraction. The stereospecific polymerization made it possible to obtain from isoprene an elastomer having chemical and steric structure practically identical with that of natural rubber.

Even if the mechanic...' and dynamic properties of synthetic cis-1,4 polyisoprene are not perfectly equal to those of natural rubber, they are fairly good and such as to allow the use of this polymer instead of natural rubber. This elastomer can be profitably produced when isoprene is available at a sufficiently low price, as in the case of isoprene already contained in the fractions deriving from crude oil pyrolysis.

The commercial production of cis-1,4 polyisoprene has already started in the United States and is justified not only by economic factors, but also by the wish for it to become independent, if necessary, of the supply of the natural product.

The use of stereo rubbers (polybutadiene and polyisoprene) is increasing every year; in 1963 the penetration of these new types of rubber represented the 8.6 per cent of the total rubber used in the United States. The consumption in 1964 will increase by 35 per cent with respect to 1963 and should be close to 150,000 long tons. In countries with free enterprise economies, the consumption in 1964 will be of 240,000 long tons. Thus market penetration on a world-wide basis will approach 10 per cent of all synthetic rubber used. In a few years, it is possible that the stereo rubbers will account for 20-25 per cent of total consumption of synthetic rubber in the United States market.

### Trans-1,4 polyisoprene

The trans isomer of polybutadiene-1,4 is the main constituent of gutta-percha; this material has been used for a long time in big amounts in the insulation of submarine cables. By stereospecific polymerization of isoprene it is now also possible to obtain a synthetic polymer having physical and chemical properties equal to or better than those of the natural product. Synthetic trans-1,4 polyisoprene is nowadays produced on a commercial scale in several countries. At present it is mainly used for the production of hard rubbers (such as golf balls), but research is in progress to widen its applications, which will be profitable considering the greater availability and lower price of the synthetic product in comparison with the natural purified one.

# OTHER HYDROCARBON POLYMERS

Along with the new polymers mentioned above, which are already produced on a commercial scale from hydrocarbon monomers, several new polymers and copolymers have been synthesized in research laboratories in these past few years, thanks to the new anionic co-ordinated polymerization processes. Some of these polymers are interesting only from a scientific point of view, leading to a better knowledge of the phenomena of macromolecular chemistry; some others, instead, are materials that at present show less practical interest, but will possibly find useful applications in the future.

Now, let us briefly consider a series of hydrocarbon polymers and copolymers synthesized in these past years to demonstrate which possibilities are given by the new polymerization processes, to obtain different materials starting from one or more hydrocarbons.

### Isotactic polystyrene

This polymer of styrene, having a high steric regularity, has a melting temperature of 240°C, while traditional polystyrene softens at a temperature lower than 100°C.

Due to its good electric properties and to its high softening point, it might be suitably used for valuable electric applications.

The practical use of isotactic polystyrene met with difficulties, due to the low crystallization rate in the moulded or extruded polymer.

### Poly-4-methylpentene-1

The isotactic polymer shows a melting temperature of 230°C; it can be easily transformed in fibres of excellent mechanical properties.

# Ethylene-butene-2 copolymers

Butene-2 does not polymerize alone in a stereospecific manner, but it can be copolymerized with ethylene. Thus ethylene-butene-2 alternated copolymers can be obtained, which show a high structure regularity and are crystalline.

# Ethylene-cycloolefins copolymers

Cycloolefins (cyclopentene, cycloheptene), in analogy with butene-2, can yield alternated crystalline copolymers with a high melting temperature and good mechanical characteristics.

# Cyclobutene polymers

Cyclobutene can yield, by polymerization, two types of polymer: one by polymerization of the double bond, the other by opening of the ring and arrangement of the units thus obtained. The latter polymer has in practice the same structure as that of trans-1,4 polybutadiene.

### Polypentenamer

By opening of the cyclopentene ring, a linear polymer is obtained, containing one double boud for every five carbon atoms in the polymeric chain. This polymer, at room temperature, is rubber-like and the vulcanized products can crystallize under stretching, in analogy with natural rubber. The good properties of these products make them particularly interesting as elastomers.

### Polymers of pentadiene-1,3

Pentadiene-1,3 can yield various polymers with different structures. Cis-1,4 polypentenamers (isotactic and syndiotactic) show an elastomeric behaviour and can be transformed into rubbers with good mechanical and dynamic properties. Trans-1,4 polypentadiene, instead, is a crystalline polymer having a melting temperature of 95°C.

# Butadiene-pentadiene copolymers

These polymers that contain butadiene as trans-1,4 units and pentadiene as trans-1,4 and 1,2 units, are elastomeric products. By vulcanization, they yield rubbers that crystallize under stretching and have good mechanical properties.

By the new polymerization techniques, it is possible to obtain *butadiene-styrene* rubbers having better properties than those of the analogous products prepared by the traditional emulsion procedures. It is also possible to produce butadiene-styrene block copolymers, which give products particularly fit for some fields of application (extruded, moulded articles, etc.).



These examples show that it is now possible to exploit almost completely the whole series of unsaturated hydrocarbons present in the volatile fractions for the production of different polymeric materials. They also show that it is now possible for the research chemist to produce the most suitable polymer for whatever application is needed.

Also in the case of polymers already known, and produced on an industrial scale, the continuous research works can lead to structure variations to satisfy the most different requirements.

# 4. NEW TRENDS IN RESEARCH AND DEVELOPMENT OF THE USSR PETROCHEMICAL INDUSTRY

### V. A. Khodakhovskaja, State Committee on Petrochemical Industry, USSR

1. At present the oil-refining industry of the USSR with respect to the volume of oil refining is the second largest in the world. During the 1958-1963 period the level of primary refining increased by 70 per cent. The rate of the petrochemical industry production growth has been even higher. From 1958 to 1963 gross output of the oil-refining industry increased more than 2.5 times. For the 1965-1970 period certain measures have been contemplated to increase further the volume of oilrefining and production of petrochemical products. During this period the volume of oil primary refining will increase by 1.6 times and production of major petrochemical products by not less than 3 times.

2. To reach the projected volume of production of mass high-quality petrochemical products, secondary processes of oil refining have been widely introduced. By 1970 these processes are to represent 55 per cent of primary refining. The following processes must be regarded as processes of major importance : catalytic reforming, catalytic cracking, hydrocracking, hydropurification, thermocontact cracking, contact coking, deparaffination.

3. The most important petrochemical raw materials are olefins, aromatic hydrocarbons and higher paraffins (liquid and solid). On the basis of these products practically all the synthetic materials are produced. The main feature of modern oil-refining is the fact that broad introduction of secondary processes makes It possible not only to settle the problem of the production of the required amounts of fuel products of required quality but to create a reliable raw material base for petrochemical production. As an example one can note the interrelation between catalytic and thermal cracking processes and production of olefins (especially, of butylenes), catalytic reforming and production of aromatic hydrocarbons, deparaffination and production of paraffins.

4. For production of olefins besides the fatty gases of cracking processes wide use is made of pyrolysis of oil production side gases and of liquid hydrocarbon raw materials—low octane benzenes of direct refining and de-aromatized raffinates of catalytic reforming. Calculations show that technical and economical characteristics of production of ethylene and propylene from liquid products of oil-refining are not worse than those obtained in production of olefins from components of side gases under condition if the use is made of pyrolysis side products (first of all hydrocarbons  $C_4$  and pyrolysis tar).

5. As far as the pyrolysis process is concerned, the main task is the improvement of tube heater design (the

principal pyrolysis aggregate for the nearest future) and creation of devices for pyrogenic refining of heavy oil fractions (mazut and raw oil including) with the aim of obtaining pyrogas of stable composition and high in olefin contents. It is not less important to work out some efficient system for pyrogas division because up to 80 per cent of expenditures on olefin production account for gas-division phase. The main direction in the creation of such a system will be low temperature rectification of pyrogases instead of absorption systems so widely used at present.

6. The olefin production gives an obvious example of a trend of steady increases in capacities of individual production units. Just a few years ago units for pyrolysis and gas-division with annual output of 10-15,000 t of ethylene were being built. At present the units of 30,000 t capacity prevailed. But in 1965-1967 standard units will be of 60-70,000 t annual capacity and in some cases (when conditions of raw material supply are favourable) - up to 120-150,000 t annual capacity. The share of such units will be about 85 per cent of total production of ethylene. Standard units for production of all the major petrochemical products will be larger. It should be pointed out that the capacity of future standard units will be at least twice as large as existing units. Experience shows that the increase of per unit capacity results in considerable reduction of capital investment.

7. The catalytic reforming process with platinum catalysts, now widely practised in the USSR, is the most promising method of production of aromatic hydrocarbons. At present the main task is to increase the yield of aromatic products per unit of starting material. To accomplish this the following measures are being carried out :

(a) Making the reforming regime more rigid and modernization of platinum catalyst. This makes it possible to use in the aromatization reactions not only naphthenic but paraffin hydrocarbons (dehydrocyclization of paraffins).

(b) Improvement of raw material preparation (deep hydrorefining, legible rectification, usage of narrow cuts).

(c) Usage of the most selective solvents at the extraction phase.

8. As far as the production of benzene is concerned the most promising processes (besides reforming process) are the processes of thermal and catalytic dealkylation, dehydrocyclization and some other processes which are being developed now. 9. The petrochemical industry now produces some chemicals which just a few years ago were produced on the base of solid fuels. Here one should first of all mention aromatic hydrocarbons. But production of aromatic hydrocarbons on the base of coking tar is limited by the scale of coke production. Special gas-chemical treatment of coal with resulting production of aromatic hydrocarbons has not yet been widely developed. This method as well as production of carbide acetylene may be only of local importance.

So in the future the petrochemical industry will be the main source of aromatic hydrocarbons and other materials.

10. The progress of the vetrochemical industry to a certain degree is stipulated by the simultaneous development of two or more processes of production of the same product or by the existence of several methods of production of interchangeable products. As an example one can point to the production of ethyl alcohol (direct and sulfuric hydration), glycerin (chloric and non-chloric method), acetaldehyde (through acetylene and ethylene), ethylene oxide (chloric method and direct oxidation) and many others. Selection of method depends on real conditions of production.

11. The simultaneous existence of competing methods predetermines the necessity for their continuous perfection. As an example one can point to the process of direct hydration of ethylene (feeding up catalyst, increase of carrier solidity, etc.), cumenic method of production of phenol, oxosynthesis, etc. Continous improvement of existing processes often explains the durability of their industrial exploitation (example — production of ethylene).

12. Nevertheless, in the industry of petrochemical synthesis great attention is paid to the development of new efficient synthesis. Here the most important trend is to substitute processes with fewer phases for multiphase processes. So as an example one can point to a recently developed process of direct oxidation of ethylene in acetaldehyde, single-phase oxidizing dehydration of butane in butadiene, production of butyrous aldehydes by the method of oxosynthesis, production of lowmolecular acids by oxidation of benzene heads, direct hydration of synthetic aliphatic acids in alcohols. Of great interest is the work on oxidation of butylene into methylethylketone, of methane into formaldehyde and some others. Practice shows that reduction in the number of technological phases contributes to considerable savings in operational and especially in capital investment.

13. Improvement of quality of monomers and intermediates is the most important condition of technological progress in the petrochemical industry. Utilization of refined and concentrated raw materials makes it possible to obtain high quality products with simultaneous reduction in expenses. As a result of pyrolysis and gas separation units now being built it is planned to operate technological systems which will provide for obtaining ethylene of 99.9 per cent concentration and propylene of 99.8 per cent concentration. Catalytic reforming and extraction units now in operation provide for production of benzene with sulfac content being not more than 0.0001 per cent. Higher alcohols now used for plasticizer production must contain not more than 0.001 per cent of sulfur. The same strict standards are now in use also for other oil-chemical products.

14. Saving foodstuffs now used for technological needs is the most important task for the petrochemical industry. Here one should point to the importance of production of synthetic ethyl alcohol, butyl and higher alcohols, dicarbon acids, etc. In this respect an important role is played by chemical working of paraffins which provides for saving a great quantity of vegetable oils and animal fats.

15. In the petrochemical industry of the USSR wide use is made of processes based on chemical working of oil paraffins. Solid paraffins have been in use since the beginning of the fifties. On the base of these paraffins we obtain synthetic aliphatic acids, higher aliphatic alcohols and other valuable products which are chiefly used for synthesis of surface-active materials. In future it is also contemplated to organize large-scale working of solid paraffins. The volume of their production is determined by the growth of lubricant production.

16. Recently liquid paraffins (temperature of melting = 20-22 °C) obtainable in the process of carbamide deparaffination of diesel oils rose in importance. This process is used to obtain diesel oils for winter and arctic conditions. On the basis of liquid paraffins it is possible to obtain practically all the products now produced on the basis of solid paraffins. Besides it is contemplated to use them for production of biologically soft alkylarylsulfonates with alkyl part of n- composition and for other synthesis where it is not possible to use solid paraffins. The main characteristic of liquid paraffins is their cheapness: their average net cost is half that of solid paraffins. Liquid paraffins can be also used as a base for the development of microbiological synthesis of such products as fodder and food albumens, amino acids, antibiotics and other microbic compounds. Utilization of micro-organisms and ferments is a new progressive trend in catalytic transformation of paraffins into valuable products.

17. Recently it has been characteristic of the petrochemical industry to develop processes for production of well-known and mass products on the base of absolutely new kinds of raw materials (synthesis of maleic anhydride from butylene, acrylonitrile from propylene and ammonia, naphtalene from oil raw materials, caprolactam and dimethylterephtralate from toluene, etc.) This trend is accompanied by considerable reduction in capital and operational expenses.

# 5. THE BIOSYNTHESIS OF PROTEINS FROM PETROLEUM

Alfred Champagnat, Managing Director, Société internationale de recherches BP

### **INTRODUCTION**

In 1957, a microbiological research organization was set up in the research laboratory of the Société française des petroles BP refinery at Lavéra. Its purpose was to find out what advantage could be derived from the microorganisms that metabolize hydrocarbons.

It was already known, and Lavéra has checked this thoroughly, that a great variety of micro-organisms live and grow actively on hydrocarbons in laboratory cultures as well as in tank bottoms, refinery oil-water separators, oil impregnated soils, and even under asphalt road pavements.

With the assistance of Docteur Jacques Senez of the Centre national de la recherche scientifique for the fundamental work, it was first attempted to make use of this microbiological action for the conversion of some oil fractions. At the time this work produced no result of industrial value. But it enabled our research team to master the technique of petroleum fermentation, and it proved that:

1. A considerable number of micro-organisms can adapt themselves to grow on petroleum fractions as the only source of carbon and energy;

2. Under suitable conditions, a certain number of micro-organisms selectively inetabolize the n-paraffinic hydrocarbons of petroleum fractions, leaving the others almost untouched;

3. By selecting suitable culture conditions, the growth of these micro-organisms on petroleum fractions is as fast as on conventional sugar media.

Two conclusions may be drawn from these experimental facts :

1. The n-paraffinic hydrocarbons found in hydrocarbon blends can be destroyed, that is to say these blends can be dewaxed. As the waxy content in some petroleum fractions, such as heavy gas oils, causes their pour point temperature to rise, those products cannot be used as fuel for diesel engines and for domestic heating. Physical ways to dewax these fractions have been known for a long time, but such methods would only throw on the market enormous quantities of waxes for which suitable outlets would be difficult to find. This disadvantage is not found in microbiological dewaxing when instead of paraffinic waxes equal quantities of micro-organisms are often produced.

2. Micro-organisms are living matter and as such are rich in proteins. This statement, which is obvious for microbiologists, made us realize that we had means at our disposal for the production from petroleum of immense quantities of proteins and a brief examination showed that such proteins contained all the aminoacids essential to life.

From then on, the objective of the research work was determined: focus all efforts on the biosynthesis of proteins from petroleum fractions, with a view to evolving an industrial process for the mass production of these proteins.

As corollary, the dewaxing of these same fractions presented appreciable prespects for the oil industry.

### STUDIES CARRIED OUT ON PETROLEUM FERMENTATION

At this stage it is appropriate to recall that many laboratory research workers have already successfully studied the culture of micro-organisms on pure hydrocarbons. But this was of no economical interest. So as to have plenty of cheap raw material available, the work had to be carried out on fractions produced by crude oil distillation.

It was in this field that the Lavéra team innovated. Whereas there is only one liquid phase in the conventional fermentation on sugar substrates, petroleum fermentation takes place in a two phase immiscible liquid medium: The continuous aqueous medium, where nitrogen, phos-

phorus, potassium based nutritive salts are to be found, as well as trace-elements and vitaminized growth

factors.

The gas oil or other petroleum fraction phase.

This is where the main difficulty arises, particularly for large-scale work.

The other difficulty is the supply of the adequate quantities of dissolved oxygen required for the metabolism. The total amount of oxygen needed for hydrocarbons is about three times as much as for sugars because the latter already contain their own molecular oxygen.

But there is an advantage corresponding to this disadvantage for twice as much cell matter is obtained when hydrocarbons are consumed as when sugar is consumed precisely because with hydrocarbons, the air oxygen is fixed on the cell matter. The nitrogen, the proteins' essential component, is supplied as ammonia or ammonium salts. It must be remembered here that ammonia is a product which the oil industry often manufactures by synthesis from the hydrogen produced by hydrocarbon catalytic conversion and from the nitrogen of air.

The chemical engineering problem was as follows: process, a four phase system: aqueous growth medium, hydrocarbons, micro-organism cells and air, in such a way that the micro-organisms are constantly able to satisfy under the best conditions their requirements of hydrocarbons, of nutritive salts dissolved in water, and of oxygen.

Also, many strains of micro-organisms growing on pure hydrocarbons had been isclated. But were these strains sufficiently selective to metabolize only the n-paraffins in blend with isoparaffins, cyclanes and the more or less ramified aromatics which make up petroleum fractions? Moreover were not these petroleum fractions poisonous for these micro-organisms? This could be wondered, as we had observed the bacteriostatic effect of a few pure aromatics on certain species of microbes.

Finally in view of the fact that the hydrocarbons wetted the lipophylic cell wall better than water, how was the final problem of separating the micro-organisms and the unchanged hydrocarbons going to be solved?

All these problems were studied in the laboratory with continuous fermentors adapted to the two phase liquid medium.

The effect of the numerous parameters governing petroleum fermentation were determined and, this is a new fact for the oil inductory, the reactions of the populations of living organism to the fluctuations of these parameters were discovered. When the appropriate value for these parameters is well chosen 1 lb of cell matter containing 50 per cent of proteins is produced from 1 lb of hydrocarbons consumed.

### SEMI-COMMERCIAL UNIT

It was now necessary to find out rapidly whether the small-scale solutions found could be extrapolated in the industry, and what would be the practical yields, as well as the actual cost of the various stages of the process.

For this, we have built a semi-commercial oil fermentation plant large enough to examine the chemical engineering problems in an easily extrapolatable manner and which also enables large quantities of micro-organisms to be produced for very thorough toxicological and nutritional tests.

This plant comprises three sections:

The fermentation;

The harvesting of micro-organisms with recovery of unmetabolized gas oil;

The purifying and drying of harvested micro-organisms.

Up to now, with the Lefrançois fermentor we are using, we have found the laws of large-scale petroleum fermentation of which the laboratory scale investigations only gave us a glimpse.

It may now be said that the technique of petroleum fermentation for the production of micro-organisms is just as advanced, as adaptable and as reliable as the main processes of the oil reliang industry. Important improvements are liable to be brought to this technique as was the case for the initial oil refining processes. But, already, we have at our disposal an extrapolatable installation for the mass production of many species of micro-organisms.

The elaboration and operation of this plant have shown us what the real problems were and how to solve them. They have also taught us what should not be done.

The harvesting, purifying and drying of micro-organisms is carried out with conventional equipment, the use of which raised many problems which have now been solved.

Other more novel solutions are of course possible, and are being examined by the BP Group. But the main thing is that we now know how to preduce, from petroleum, micro-organisms rich in proteins.

There are many ways of using proteins, from the dried micro-organisms to the pure amino-acids, including the polypeptides of various degrees of purity.

Petroleum fermentation is paving the way for the production of all these varieties of protein concentrates.

### PROTEINS

Having briefly touched on the experimental work carried out at Lavéra, we shall now attempt to compare the petroleum fermentation proteins with the others from the quality and quantity angles.

Proteins are part of both animal and vegetable life. So far no synthesized proteins have yet been produced without a living germ.

Petroleum fermentation proteins are just as natural as those of vegetables and animals, for they form the essential element of the micro-organism cells that have learned to take their carbon from hydrocarbons rather than from sugars or carbobydrates. This adaptation took place without appreciable mutation. In particular, the amino-acid pattern in proteins of micro-organisms grown on petroleum is the same as that of proteins of the same species grown on conventional sugar substrates. We have examined all these amino-acid's in our own laboratory and found them to be laevorotatory.

# HOW PROTEINS ARE GROWN

Because we shall rapidly examine the various ways in which proteins are grown, the sketchy nature of this report leads to overshort generalizations and to insvitable omissions.

### 1. Vegetable kingdom

Here proteins draw their carbon from the carbon dioxide in the air, by chlorophylic assimilation, and the nitrogen, phosphorus and potassium elements from the soil to which the necessary fortilizers are added to obtain estisfactory yields without it being exhausted. Water and sunlight are essential. Lastly, the sun supplies the energy consumed for vegetable growing. The vegetable proteins are found in seeds, leaves stalks and roots. Most non-ruminani animals and human beings only assimilate the proteins in seeds and in some roots or tubers.

The production of agricultural proteins depends on the soil, the climate, rain or irrigation system. It requires fertilizers and plenty of qualified labour

Among the vegetable proteins those of cereals play the most plentiful part in the diet of the world's population but their amino-acid pattern is badly balanced Lysine is generally deficient as is methionine and/or triptophan in some cases so that their biological value is reduced accordingly Leguminous proteins soya beans, haricot beans, chick peas, etc. have a better balance and the same applies to those of some oil-cakes made from the extraction of vegetable oils

Grain blends having a suitable biological value with or without oil-cakes can therefore be made, and this is a very important source of sumply on world-wide basis. A process is being developed which will enable proteins to be extracted from leaves and even from stalks.

### 2 Animai kingdem

Ruminant animals make their own protein from the vegetable material by using the paunch of their digestive system. In fact the action of certain micro-organisms in this organ produces a biosynthesis of amino-acids

Non-ruminant animals have no such facility and consequently for their growth and to maintain their nitrogenous balance they must eat vegetable or animal foods which already contain these essential anino-acids. Nonruminant animals do not generally assimilate proteins from leaves. In stock farming, such animals can live on grain proteins providing they eat an adequate amount. But balanced foods containing sufficient quantities of all the indispensable amino-acids produce much better results. The elements required to keep them alive, notably nitrogen in the shape of mineral salts or elementary organic compounds, cannot be directly assimilated by animals with the exception of urea and some ammonium salts, but it does not seem that they could be used for feeding on a universal scale

Consequently stock farming depends on agriculture, and the production of animal proteins is costly because of the intermediate agricultural stage and the inadequate yield of animal biosynthesis. Seven calories of carbohydrates are required to produce one calorie of beef proteins and three and a half to produce one calorie of chicken proteins.

Live-stock raising is directly or indirectly dependent on the nature of the soil, on the climate, on water, fertilizers and labour. Diseases or tropical insects can also make it difficult or impossible. In general, the area outside the tropics, where the problems of malnutrition do not normally occur, are those where stock raising yields are the best.

We must not forget that fresh water fish and sea weter fish are a source of supply less affected by climates and can be increased in the tropics where proteins are lacking. Many insects could and, indeed in some countries, do form a plentiful source of excellent proteins. Although the raising of insects would not appear to be carried out in a realistic way, this possible source of supply should be borne in mind.

### 3 Micro-organisms

Micro-organisms are included in the vegetable kingdom and this fact is important as, from a religious or customary point of view, there is no objection to their being consumed. Apart from some of them which thrive on the carbon dioxide of air, they usually obtain carbon from carbohydrates, mainly sugars, and like vegetables they directly assimilate the nitrogen, phosphorus and potassium elements in the shape of mineral salts or organic compounds.

But they constitute immense possibilities for the production of proteins, because of their high nitrogen content, and because of the rate at which they grow. The generation time of a micro-organism cultivated under optimum conditions is 2 to 8 hours, in other words, its weight doubles every 2 to 8 hours. This is several thousand times as fast as that of the protein synthesis of beef raising for example.

No soil is required for the cultivation of micro-organisms, nor does it depend on climate, rain and plentiful labour. It takes place in an industrial apparatus operated by small teams of technicians. It therefore corresponds to a kind of soil-less cultivation with extremely high productivity, or to intensive stock raising such as that of pouliry but with two advantages. a much faster production and direct assimilation of chemical fertilizers.

Properly dried, the micro-organic cells burst open and thus become more digestible. They can be preserved for long periods if precautions such as those for flour storage are taken

The production of micro-organisms for feeding purposes has been a conventional industry for a long time now, such as the case of yeast for animal feeding and human dietetics. Their proteins resemble animal proteins, and furthermore they contain large quantities of growth vitamins.

So far, micro-organisms for feeding purposes have been cultivated on sugar substrates: molasses, residuary wine :aking liquors, residual paper mill lyes. There are plenty of these substrates in the world but they are unevenly distributed.

The new prospects which petroleum formentation makes possible for the cultivation of micro-organisms are now poing to be examined.

### PROSPECTS OF THE DEVELOPMENT OF PETHOLSUM PERMINITATION

It has been said that the technical process as it now stands will certainly be improved in time, as experience in the oil industry gives reason to expect. But there are other means of progress.

A considerable number of micro-organisms are able to grow on petroleum substrates. Only a few species have been studied. The best micro-organism or microorganisms for the production of proteins with the best yield or with a fast growth may be chosen for each of the petroleum fractions. The quality of proteins in each species of micro-organism varies from one to the other. It would seem that "made to measure" proteins could be produced by selection or genetic means for the supplementation of one cereal or the other.

The nature and proportion of the components of micro-organisms other than proteins: lipids and carbohydrates also vary according to the species and methods of cultivation. The range of possibilities is therefore immense, more so than for live stock raising and agriculture.

Daniele Bovet (1) has said that in the 14th century, the yield of wheat cultivation in England was 430 kg per hectare as against 3,500 kg nowadays. The huge steps made in a few years in the production of antibiotics through necessity and with modern methods, are also an example and an encouragement for us all.

The BP Group is devoting a considerable effort to petroleum fermentation. For example, apart from the BP development centre at Lavéra, another one has been installed at Grangemouth in Scotland and consideration is being given to the establishment of pilot-scale animal feeding trials under tropical condition in Nigeria, where the petroleum raw materials needed for the production of protein concentrates are available at the Port Harcourt Refinery.

Finally, the fundamental aspects and the application of petroleum microbiology are to be thoroughly studied in a laboratory specially set up for that purpose in the Paris area by the Société internationale de recherches BP.

Apart from the BP Group, other research centres and leading oil firms in several countries are following in our trail. All these efforts will produce positive results much sooner than may be expected.

### PETROLEUM AS A SOURCE OF PROTEINS

What has just been said about the possibilities of progress in petroleum fermentation is equally valid for the conventional fermentation of sugars and it is desirable that this should be done in that branch. But the oil industry benefits from an actual situation which enables it to succeed both in research and in mass production. Crude oil, although perhaps not the most abundant carbonaceous material, is undoubtedly the most easily distributed one in the world through gigantic oil tankers fleets. Compared with the other main basic materials, its price changes but little. It is relatively low for it is a source of energy which is universally used. Finally, it is appreciably the same all over the world.

Over 700 refineries, set up in all countries, form a readymade structure to which fermentation units, that at the same time can be dewaxing units, may be added.

The oil industry, an international one, concentrated into a small number of powerful and well organized firms, possesses all the essential conditions to quickly produce vast quantities of stable quality low cost products. Using as a basis the 1962 production of cru'e oil, about 1,250 million tons per annum, we have calculated (2) that the potential production of pure proteins could (each 20 million ton: if required by using not much more than 40 million tons of petroleum products. The ammoniacal nitrogen required for this production only represents a very small fraction of the present world production and, moreover would, no doubt, also be manufactured from oil, in the same way as large quantities are already being produced. These very great production possibilities justify the efforts made.

# NATURE OF PETROLEUM PRODUCED PROTEINS

The most attractive commercial form seems to be the dry and exploded micro-organism resulting from the manufacturing process explained earlier. This type has been called protein-vitamin concentrate.

The protein content of micro-organisms varies very widely from 30 to 80 per cent. The experience that has been gained makes it possible to count on at least 50 per cent, a figure which could well fluctuate with the type of micro-organism used and with the culture conditions.

Next to the proteins, the lipid content of protein concentrates may be limited to 5 per cent and even drop to 1 per cent according to requirements.

The unsaponifiable compounds are present in a quantity that Joes not exceed their usual one in conventional yeasts, in fish meals, etc., i.e. 1 to 2 per cent.

The nucleic acids, the mineral elements and the carbohydrates found in protein concentrates do not seem to be in any way different from the same constitutive elements of conventional yeast cells for instance.

Hydrosoluble vitamins, mainly those of group B, must be specially mentioned. Growth vitamins are present in quantities that, for some such as riboflavine, largely xceed their usual proportion in the same micro-organisms grown on sugars. Next to those vitamins which have been identified, there are still unknown natural factors, the growth value of which in conjunction with proteins has been acknowledged in the case of conventional yeasts (3).

### NUTRITIONAL ASPECT

The in vivo rate of digestion of protein-vitamin concentrates in rats depends on the manufacturing processes which make it possible now frequently to obtain values of 85 to 90 per cent. As everyone knows, this corresponds to the percentages of nitrogenated substances assimilated by the animal.

The biological value of micro-organism proteins is not as high as that of true animal proteins. It varies with the species of microbes as a function of the pattern of essential amino-acids. The micro-organisms that we have studied so far are very rich in lysine and are deficient to a certain extent in sulphuretted amino-acids, methionine end cystine, with a respectable dose of tryptop han. With this composition protein-vitamin concentrates become a choice protein substance for supplementing cereals. Cereals contain 6 to 12 per cent of proteins, sometimes

more. This is an enormous amount on a world scale. Cereals being the basic food of most peoples, the problem of nitrogenated nutrition would not be so acute if cereal proteins had a sufficiently high biological value. Unfortunately, cereal proteins are largely deficient in lysine and sometimes in tryptophan. Their biological value is lessened owing to this and so only a small proportion of the available amino-acids is used by the organism for the production of its cells. Cereal proteins generally contain enough sulphur containing amino-acids. It would therefore seem that the judicious use of proteinvitamin concentrates from petroleum is the supplementing of cereals since their amino-acids are complementary to each other. Owing to this, cereal proteins could be improved by adding from 2 to 10 per cent of proteinvitamin concentrate. For each existing cereal, there is an optimal supplementary dose, and we consider that it would be possible to produce protein concentrate "to measure" for each one.

This method of improving imperfect proteins is the work of nutritional experts. We have acknowledged the great interest of this and we shall apply it in the choice to be made of the micro-organisms to be cultivated on petroleun.

It follows from what has just been said that proteinvitamin concentrates will not in themselves form a balanced food and one must not think of using them at doses exceeding 20 per cent (corresponding to 10 per cent of pure proteins) in compound foods, the remaining protein ration needed being vegetable proteins. Furthermore, stock farmers know how good it is to combine various animal and vegetable proteins. The association of fish meal and conventional yeast, for instance, has produced excellent results by supplementing conventional cereals.

Finally, it can be stated that when micro-organism proteins are correctly associated with cereal proteins, the blend has a biological value similar to that of animal proteins and we consider that, from a total quantitative point of view, it is possible to reason as in the case of animal proteins.

### TASTE AND SMELL PROPERTIES AND ACCEPTABILITY

Properly purified dry micro-organisms appear as powder or as white chips; they are odourless and have no appreciable flavour when they are sufficiently free from lipids. It goes without saying that it is not possible to detect the taste of petroleum in them. This neutral taste is capital for their acceptance. As it has been explained there is no question of consuming them as such, but of incorporating them into cereal based conventional foods in order supplement the protein in such cereals.

Their incorporation into cereal flour could be carried out at the sufficient dose of 2 to 10 per cent in order to raise both their biological value and their total protein content. Checks have shown that such doses do not in any way prevent panification. The preparation of sweet or salted biscuits has also been studied. Biscuits containing from 20 to 40 per cent of protein-vitamin concentrates have been made, without milk, without eggs and with the fatty substances available in most undernourished countries. These biscuits have a pleasant taste. It has thus been demonstrated that petroleum proteins are fully acceptable at least when they are presented in this way.

Lipids in protein-vitamin concentrates may be allowed to appreciably remain, which is an advantage for feeding live stock. They have then a slight and not displeasing odour and a sweetish flavour that animals seem to like, and which are certainly far less strong that the smell and flavour of fish meal.

### AUTOLYSATES AND HYDROLYSATES

The autolysates and hydrolysates of micro-organism cells cultivated on petroleum have been studied. As is known, these techniques consist in bringing about a kind of pre-digestion of the cells with the help of their own enzymes, with external enzymes or with acids or alkali. The walls of the cells are separated. The protein chains are broken and go into solution. The lipids and the unsaponifiable elements are easily separated.

These methods are widely used in the food industry for the preparation of meat, fish and yeast extracts, the utilization of which has become customary.

The micro-organism autolysates and hydrolysates cultivated on petroleum have different flavours according to the species, the enzymes used and the methods employed to make them. In particular strong flavour autolysates have been produced which closely resemble the nuocman appreciated in Asia.

The choice of possible flavours is great and this opens up horizons which will undoubtedly be exploited one day.

But another advantage is the great digestibility of these products, without the cellular walls, the lipids and the unsaponifiable elements.

Even if the dry powder form gave rise to reservations, the range of the corresponding autolysates and hydrolysates would introduce a decided improvement. The transformations can even be carried to the point of obtaining pure polypeptides which would be a vegetable meat, the consumption of which would not give rise to any objection from hygienists.

But amino-acids are delicate. In such transformations, the aim of which is to obtain attractive and palatable shapes, we are not giving in to the temptation of elaborating products that would be a sure commercial success in their presentation, if this were to be at the expense of their nutritional value.

### TOXICOLOGICAL ASPECT

Owing to the importance of the potential production of proteins by petroleum fermentation we received the encouragement of scientists and of economists from international organizations. Such encouragement was accompanied by the justified wish to develop wide-spread toxicological experiments. This is also our main preoccupation and concurrently with the pursuit of our technical effort, the protein concentrates made by us are submitted to specialized laboratories which study the effect of their incorporation into the diet of animals. But for such tests to acquire an unquestionable value they must be continued over a long period of time.

The observations that have been made guide us in the selection of the manufacturing process variants and in that of the micro-organisms. These experiments will be carried out on a large scale now that our semi-commercial plant is quite ready for the production of great quantities of protein-vitamin concentrates.

When the time comes, we shall submit our final products to the laboratories approved by international organizations so that all necessary tests may be carried out.

In this respect, we would like to stress that the longterm effort made in this field is extremely costly and that our success will open a door through which others will pass at less cost than we have done.

Finally the long delay required for valid toxicological studies should be considered as an example of the extreme care which we are taking to ensure the success of our work and not as an indication of inability to proceed faster.

# ECONOMIC PROSPECTS

Assuming that all the toxicological and nutritional tests have been successfully achieved, what does the 20 million ton potential of pure petroleum proteins represent? The present production of fish meal is 3 million tons per annum and this corresponds to 2 million tons of pure proteins. This gives an idea of the importance of the new resource.

This figure of 20 million tons is the result of arithmetical calculations and this does not mean that it is commercially possible nor imminent. A considerable effort will have to be made and the growth in population will perhaps be the determining factor towards materializing the possiblities of petroleum fermentation.

If one thinks about the amount of work and money that would be needed for the rapid production of an equivalent quantity of animal proteins through conventional methods, stock-raising and fishing, one is nevertheless struck by the greater ease of this production from petroleum.

In support of this assertion we would mention H. D. Kay (4) according to whom it is neither the lack of our knowledge of the fundamental sciences nor that of the requisite practical methods to apply them in the fields of agriculture and dietetics, which constitute the major obstacle to the improvement of the nutritional level in most of the undernourished countries, and this despite their excessive population increase. It is rather more the extremely slow circulation of this acquired knowledge, which is caused by political, sociological and physiological obstacles that no technique has so far been able to overcome.<sup>1</sup> Next to that, the powerful and dynamic oil industry concentrated into a small number of firms is quite capable of organizing itself in a relatively short space of time to produce proteins, in exactly the same way as it became organized for the production of chemicals. This would represent a new diversification and everyone knows how the need for diversification is making itself felt in industry at the present time.

Oil is a fossil matter and is therefore not inexhaustable. Authorized opinion, however, stresses the importance of the proven reserves which increase every year, and of the still unproven ones under the sea beds and which it is now possible to prospect and exploit. Added to oil, the bituminous sands and shale fields will ensure an adequate supply of hydrocarbons for a long time yet.

It is interesting to recall, with Daniele Bovet (5) that "the total energy of all the foods consumed by mankind represents only about 13 per cent of the energy produced by oil, coal, gas and water power". This ratio between food substances and energy should remain fixed in the minds of the economists and, more especially, in those of planners, for it would be presumptuous to increase the available energy if the availability of food substances is not increased at the same rate.

# UNDERNOURISHMENT AND PROTEIN REQUIREMENTS

The effects of protein deficiency are well known but it is nevertheless necessary to stress one of their aspects.

Hunger diseases are essentially due to a shortage of proteins and result in physical weakness an in intellectual misery which causes those who suffer from them to lack the ambition and the energy to remedy their condition. Should they wish to, they would be lacking the necessary physical stamina to do so. Alongside with the sociological and political obstacles mentioned by H. D. Kay, and which we do not intend discussing here, this physiological and psychological situation is an ill which can be cured by foods sufficiently rich in high value proteins.

The supply of these proteins should be considered as a therapeutic treatment to give man this strength and energy to adapt himself to modern methods of cultivation to increase food production. It should also give him the possibility and the will power to reform ancestral habits of a badly balanced diet which play a large part in the causes of malnutrition. One example of this therapy is that of the treatment of Kwashiorkor with milk proteins which are unfortunately unavailable in adequate quantities.

Petroleum proteins, from the day when they will be considered and accepted for human consumption, could help much in this respect. But, they could contribute much more quickly to greater animal protein production by helping to develop live-stock raising.

### QUANTITATIVE ASPECTS OF THE PROBLEM OF ANIMAL PROTEINS

Our first papers mentioned quantities that were clearly too small for world needs of animal proteins. They were

<sup>&</sup>lt;sup>1</sup> We would put the proposition forward, that it is not shortage of basic scientific knowledge nor of sound and practical methods for applying it to agriculture or distetics that is the great obstacle to improvement of nutrition in most of the kungry countries, even with their present excessive rate of growth of population. It is rather the extreme elowness of implantation of the knowledge, a slowness caused by political, sociological and physiological obstacles to overcome which effective techniques have still to be found.

circulated through the press which even went so far as to imagine that petroleum proteins could one day resolve the problem of protein deficiency.

Since then we have become acquainted with the remarkable study by P. V. Sukhatme (6) and this has enabled us to assign a place to petroleum proteins in relation to present and future needs.

The attached table does not form part of the work of this author who deals with world food requirements without concentrating only on animal proteins. But the figures quoted are all contained therein. They have been grouped in condensed form and the individual rations quoted have, in this case, been multiplied by the estimated population on various dates chosen so as to obtain the corresponding tonnages of pure proteins.

Sukhatme has given average figures for two groups of countries. The first group comprises the Far-East, the Near-East, Africa and Latin America excluding the Rio de la Placa countries. The food position in this group is very precarious and needs to be seriously improved.

The second group comprises those countries in which there is no food problem on the whole. It includes Europe, North America, Oceania and the Rio de la Plata countries.

The estimates have been based on 1958 figures in regard to population and protein rations.

First of all, targets for the improvement of protein rations were given for 1980 and the year 2000 in countries of the first group. Allowing for the expected population increase at these periods, the tonnage of animal proteins required to satisfy such needs during these periods have been calculated. It has also been assumed that the countries of the second group would not seek to improve their present  $\tau$  cions which are already over abundant.

Finally, the third column lists the world needs. It is almost superfluous to add anything to the eloquence of these figures. A production of petroleum proteins estimated at 20 million tons per annum would in 1958 have been equal to the world production and could have substantially improved the rations of the first group of countries. But the position is no longer the same at the present time and the 20 million ton production of petroleum proteins is a distant objective. It would already be very comforting if 3 million tons could be produced in the next few years, and the disproportion in relation to needs is then unquestionably apparent.

If one takes the 1980 level as a more reasonable one and by still assuming that petroleum proteins would be a success, their contribution may be considered as interesting, for they would represent about half of world needs, and this would relieve the huge effort to be made in the production of conventiona! proteins.

But, for the year 2000, and specially owing to the growth in population, the relative contribution of petroleum proteins then only equals one third of the needs, unless scientific and technological progress makes it possible to increase their production. This hypothesis seems rather unlikely for, in any case, one day or another, it will be necessary to use sparingly the fossil resources available to man. It is therefore with modesty that we must consider what our work contributes when faced with the immensity of the problem. It is also a reason to persevere and to hope that the research work being pursued in other directions for the production of non-conventional proteins will succeed. The figures that Sukhatme quotes makes it obvious that there will never be competition between the various proteins for the conquest of outlets which become increasingly greater each day. This is what we are trying to prove to the managements of some food industry firms, where concern is being felt about possible competition from petroleum proteins.

### **CONCLUSIONS**

During the years ahead, it is the growth in population that will aggravate the already unfavourable world food situation. The main unknown elements are the time that it will take to reach an equilibrium level and the corresponding world population figure. Despite the appreciable

### ANIMAL PROTEINE

Availabilities in 1958 - Present and future requirements

	Int group * countries	Ind group b sound-les	World
Position in 1958			
Population in millions.	2,001	858	2,859
Available animal pro- teins			
Grams per day per capita.	9	44	20
Available animal pro- teins in 1,000 T	6,570	13,880	20,450
Improvement object- ives		·	·
Grama per day per capita, 1980	16	42.7	24
Grams per day ner			
capita, 2000	20	43.3	27
Total population *			
19 <b>80 (millions)</b>	3.117	1,103	4.220
2000 (millions)	4,935	1,332	6,267
Needs corresponding to the improved rations and to the population increase			
1980 (in 1,000 T).	18,850	17,300	36.150
2000 (in 1,000 T)	36,500	21,500	34,000

Processing Proof: Succession, The World's Sunger and Pursue Needs in Pool Supplies (PAO 1961).

· ist Group: Per Best, Near Best, Africe, Letin America enduding The Ris do in Pista countries.

\* 2nd Group: Buropo, North America, Ossanin, Rio do la Plate countries.

. United Nations 1995 mean hypothesis.

contribution of petroleum proteins and no doubt very soon of other non-conventional proteins, it should be appreciated that only direct or indirect agricultural resources are permanent and renewable, for in point of fact their occurrence is possible through the sun's energy.

It is in this direction that long term research should find a fertile field of action. The production potential of life, which supplies proteins, is much greater than one usually imagines. And it is up to science to know how to exploit such possibilities, principally to the biological sciences. Daniele Bovet teaches us (7) that the order of magnitude of terrestrial living matter is equal to a 10 cms thickness spread equally over the entire surface of the globe. The human population uniformly distributed over the surface of the emerged lands would form a layer of less than two thousandth of a millimetre. Furthermore each year mankind, in order to feed itself, only consumes an extremely small fraction, about 1/10,000th of the theoretically available organic matter.

Science has therefore sufficient renewable raw material to provide mankind with the nitrogenous substances required for its survival; on the condition that we want to rid ourselves of our intellectual routines.

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# 6. UNESCO AND THE TRAINING OF MANPOWER FOR THE PETROCHEMICAL INDUSTRIES IN DEVELOPING COUNTRIES

UNESCO, Department for the Application of Science to Development

# I. UNESCO'S CONCERN WITH TECHNOLOGICAL TRAINING

The problem of the development of petrochemical industries in developing countries is closely connected with the availability of the necessary trained manpower to carry out all development plans which can be conceived by the petroleum and petrochemical experts of the world. UNESCO, the United Nations Educational, Scientific and Cultural Organization, is committed to assist in the training of skilled manpower and, as the member of the United Nations family specifically dedicated to educational and scientific pursuits, is glad to contribute to the discussion of this inter-regional conference.

The concern with the training of technical personnel and with all vocational and technological education which is one of UNESCO's most important functions, stoms from the very obvious and ever-increasing need for large numbers of technical personnel for all industries. The United Nations Committee for Industrial Developmont shares with UNESCO an awareness of the terrible handicap which so many Member States and nations of this world must remediate by educating large numbers of their people so that they can play a part in their nation's technical advancement and industrial progress. The very history of the advancement of certain nations in this world is extremely closely connected with the availability of multitudes of trained personnel which can man the offices, workshops, laboratories and factories: they all together constitute the network providing the national comonny with its progressive character.

The utilization of natural resources is of course the original and most important aim of all endeavours which concorn the nation's living standards; their study, conservation and utilization must be the object of both research and personnel training in the above connexion. New one of the most important natural resources of the developing countries is undoubtedly petroleum and natural gas and the subject of this Conference, namely the production of petrochemicals is inseparably connected with the utilization of petroleum and gas resources. The organizations participating in this conference have prood numerous statistics and other evidence showing the constantly growing knowledge we have today of the jobe's reserves of these two important fossil materials. Many new reserves are now being discovered everywhere on the continental shelves surrounding the land masses of our continents : with increasing discoveries of petroleum

reserves we can be equally optimistic regarding the future availability of petrochemicals made therefrom. Latest statistics seem to indicate that of all organic chemicals produced now in all countries of the world, 85 per cent are manufactured from petroleum derivatives as their raw material. These fundamental facts alone warrant close attention to petroleum as one of the globe's most important natural resources by all who claim to be concerned with technological progress.

While UNESCO's action in other scientific fields (e.g. hydrology, seiamology, oceanography, life sciences) and in connexion with other natural resources has been well established for many years, its activity in the petroleum technology and in the training of technologists and technicians for the petroleum industries is rather recent. However, it is increasing very rapidly, in particular thanks to the Special Fund, and we are therefore grateful that we can clarify our own possible part in this area at the present Conference.

### II. TECHNICAL PERSONNEL FOR THE PETROLEUM AND PETROCHEMICAL INDUSTRIES

The educational statistics available with us for developing countries unfortunately do not permit us to have a very clear idea of the manpower needs concerning the developing nations with reference to petroleum progress and petrochemicals. Going from country to country where in recent years oil fields and petroleum refineries have sprung up, the evidence points everywhere to a very obvious lack of the necessary local personnel. Expetriates from the major industrial countries have almost everywhere started the petroleum endeavours, and foreigners, in many cases Americans and Europeans or Japanese, have acted as leaders of slowly growing teams of local technicians' and technologists who have exploited the developing countries' petroleum resources. However, the exact need for teshnical personnel remains even now completely undefined because of the absonce of reliable statistical figures.

Engineering survives and a world survey of technical education can be attempted on the basis of individual investigations from country to country. When in a recent case a UNESCO enquiry in one of the Middle Eastern countries led to a request to the United Nations Special Fund for the financing and organization of a new petroleum institute, it was possible to give some rudimentary figures on the country's graduated engineering students and trained employees working in that nation's petroleum industry. However, as a complete picture of the world's needs of petroleum technologists and technicians, all we can produce today is a very sketchy outline, and verification from place to place must still be undertaken at a future date before we can authoritatively summarize the manpower needs of the world's present petroleum industry, not to mention the much more considerable needs for trained petroleum people in the future. We are very much concerned with this specific lack of information because it is of course realised what an immediately important natural resource is constituted by petroleum and natural gas in many nations of the globe.

In the petroleum industries, responsibilities of technicians and technologists often overlap, and it is a very difficult task in itself to formulate generalizations regarding the separation of these two categories, and again to assess figures for these two categories of manpower as against the total labour force employed in petroleum endeavours. As an approximate figure we find that 25 technologists and technicians are corresponding to a labour force of a thousand in an average developing country. However, the length of pipelines, the depth and nature of the individual deposits, the lack or availability of harbour facilities are all so different from country to country that such generalisations are often valu less. Another matter to be mentioned here is that quantities are in reality not the main criterion when technologists and technicians are discussed for any particular industry: it is the quality of the men, their specific individual contribution to the progress of the exploration and exploitation of the resources which matters in the daily routine of the work to be accomplished. One high-class engineer with many years of experience can often provide better leadership than several trained graduates of engineering schools whose combined petroleum experience does not equal that of a high-class specialist.

Within the technologists, certain categories are indispensable because their specific tasks after appropriate training do not overlap. No oil field work can be carried out without geologists and geophysicists. Reservoir engineers have their specific tasks which are entirely different from those of the refinery engineers concerned with crude processing. In turn, chemical engineers for the petrochemical processes have to apply their specific training and cannot be replaced by mechanical or civil engineers if useful products are to be manufactured from the natural gas or crude petroleum products as they arrive at the petrochemical plant in the form of streams of petroleum derivatives. Technical universities are today a source of the technical training which all these specific categories of technologists must receive, but the big petroleum companies must very frequently add to the formal training received at school by their technologists in order to make these men immediately useful for tasks in the field. When the curriculum of training courses in specific petroleum institutes is set up it must be kept in mind that the graduates from these institutes must include mon corresponding to all the shove and several other categorist. To cover with all detail the requirements for modern petroleum technologiets which are today

standard practice in every oil field, petroleum refinery and petrochemical plant, very detailed planning of the corresponding educational facilities is indispensable.

On the other hand petroleum technicians who are not academically trained should if ever possible have an all-round background so that they are able to fulfil a multitude of tasks in their intermediate position between the professional technologist and the labour force. In this connexion, the general educational level of the available trainees must be very carefully considered: local primary and secondary educational standards vary, but a petroleum technician must undoubtedly in every case be a literate man with satisfactory human qualifications in addition to his formal knowledge. It is of course impossible to apply everywhere such simple checks as for instance are provided by the "I.Q." (intelligence quota) standards aptitude tests for mechanical and general abilities. But each trainee must be individually considered, and certain common features must be encountered to make a man into a satisfactory petroleum technician: alertness, responsible attitudes to team-work and to accident prevention are prerequisites. One may even go further and insist on some pro-scientific inclination, on a check on sobriety and on generally modern personal attitudes such as are often not encountered when people of very primitive living standards are considered for training. Youth may be generally considered as an advantage, as on-the-job training of older people presents additional difficulties. Furthermore, in developing countries it will normally be necessary to train in the first instance only men even for laboratory and other work which, in the more developed countries, is often carried out by female workers. The training of petroleum technicians must also include instruction in general subjects. Like all other training, petroleum training according to general views contained in many UNESCO publications aims at improving a skilled labourer so that he can assume both technical and human leadership and show his own initiative wherever required. Of course, a petroleum technician working mainly as a laboratory control specialist need not be too familiar with the tasks of the reservoir technician, for instance tank strapping. The technicians in the gas field will have many individual experiences which are of little concern to the operator of a petrochemical still. However, the curriculum for technicians in petroleum institutes should be planned in such a way that sight is never lost of the co-ordination and interplay of all technical matters including petroleum and petrochemicals. This is also in the interest of the individual technician who should not become too mucii of a specialist but remain interested in the general layout and progress of all the technical work around him.

Coming finally to the researchers there will of course be specialists and professionals with their determined definite tasks. In this area it will be unavoidable to have men devote long periods of their lives to their clearly defined specific research subjects. It is evident that in the petroleum industry there are research problems concerning for instance instrumentation and instrumental analysis, or knowledge of engine evaluation in connexion with fuels and lubricants which can only be furthered by highly skilled individuals. The same applies to the field of seismic exploration and of geo-physics in general, to catalytic refinery processing and to the study of additives, just to mention a few specific research subjects of concern to the petroleum industry. When determining the organization of petroleum institutes which should at the same time perform training and research tasks, these needs must not be overlooked: experienced petroleum specialists must be called in from the industry and the planning of buildings and laboratories, as well as the availability of training and research equipment and staff must be the responsibility of petroleum and petrochemical experts to make such a petroleum institute satisfactory for all the meeds which must arise during its proper functioning.

### III. TRAINING OF TECHNICAL PERSONNEL NEEDED IN DEVELOPING COUNTRIES

The problems of developing countries differ in many aspects from those encountered in the advanced countries and the establisher of training facilities must take specific account of all the ponderable and imponderable difficulties influencing both the trainers and the trainces. The petroleum and petrochemical industries have been originally developed with the help of personnel whose general standards of learning and everyday living were the results of centuries of educational advancement. Even where backward areas of, for instance, the United States were developed as petroleum producing areas, there was an abundance of literate and highly qualified craftsmen at work to accomplish the multifarious tasks. In developing countries this backlog of generally trained craftsmen is normally in abeyance. The general reasoning of a personnel manager who has dealt with refinery or chemical plant personnel in, for instance France or Rumania or Canada, does not apply at all when the same official has to cope with the personnel needs of exactly the same technical production facilities in Central Africa or a backward area of Asia or Latin America.

The oldest petroleum refineries in developing countries were relying to a great extent on personnel trained abroad. In addition to expatriates the oil industry normally took immediate steps to provide technical schooling for a sufficient number of nationals of the particular country in training facilities abroad. The availability of excellent and highly specialized training for petroleum men and petrochemists in such states of North America as Oklahoma, Texas and California permitted the enrolment of relatively large numbers of foreign students who shared the benefits of this special training with nationals of the United States before they returned to their countries to take up jobs in the field.

Training abroad does, however, involve a very considerable amount of risks. The first barrier which a trainee has to overcome is in most instances the language barrier. Even if language training has been provided at home it takes a foreign student a rather long time before he can fully benefit from training provided to him in a foreign language. Furthermore, the human environment very often differs so strongly from the trainee's home environment that the period of acclimatisation is normally quite long. A further danger consists in the completely different personal outlook which many students from developing countries gain once they are exposed to routine life in advanced countries: many take advantage of the growing labour markets in the countries of their training to postpone returning to their home base. UNESCO has had a recent conference in Lagos which *inter alia* discussed this aspect of training abroad for Africans in considerable detail, and another specific aspect which the Lagos discussions brought out was the question of "status" and its implications.

The obvious answer is to provide training right in the developing countries. UNESCO has been set up by the world's governments to act somehow like a giant international ministry of education and all problems of primary, secondary and university education are currently and constantly discussed by the local governments with UNESCO officials. It is, therefore, natural that UNESCO is familiar with all existing universities and polytechnic institutes. So it is logical to look at these training institutions for help also with reference to the training of manpower for petroleum and petrochemical industries.

In developing countries, however, the original universities and technical institutions are of course normally not specialized enough to provide the training with which we are concerned for specialists assuming responsibility in the petroleum and petrochemical industries.

There is, however, a possibility of providing specific experts and also fellowships so that the existing universities and polytechnical schools can offer petroleum and petrochemical courses. UNESCO has been able to institute just this kind of training in several developing countries. Petroleum engineering courses are now being given under the auspices of UNESCO both in Africa and Asia and we hope to develop standard procedures and to convert many more existing academic institutions into training centres for specialists in the fields of petroleum technology and petrochemistry.

Of course the raw material with which we are concerned is of a specific nature in so far that its discovery normally initiates a sporadic effort to arrive as fast as possible at exploitation. No need for petroleum specialists appears to exist in any developing country before oil or gas is struck: on the other hand, as soon as a discovery is made the economists of a developing country are most anxious to proceed with exploitation as fast as possible. Most frequently they are assisted in this endeavour by people from abroad who are laying the foundation stones of a future industry but who in turn immediately need assistance from local nationals who can be taught to take over the various responsibilities from the expensive foreign specialists. These must be sent home and cannot be employed for too long a time if petroleum exploitation is to remain profitable.

A so-called crash programme is, therefore, often considered essential and training of sufficiently large numbers of technicians and technologists is planned in the shortest possible time. The results of this are very often disastrous because there are no short-cuts to fundamental knowledge of the necessary techniques and sciences needed to run a successful petroleum and perrochemical industry. It is logical that the governments of developing countries must be mainly concerned with the long-range effects which the availability of these natural resources in their soil can have on the economy and welfare of their people. Training must be profound and the petroleum and petrochemical specialists must be up-to-date on all modern techniques and really and truly specialists familiar with all angles of their calling to be of permanent value to their nations. UNESCO is theoretically opposed to half-measures such as a crash programme would involve.

On the other hand, long-range planning will often result in dissatisfaction with the possibilities offered at existing schools. Looking closely at the laboratories and training personnel normally available as a nucleus on which petrochemical and petroleum institutions can 'e based, it soon becomes evident that in many places there is bound to be a waste of effort and unsatisfactory results if UNESCO confines itself to send professors and experts and to provide fellowship at existing institutions. The answer to the needs of petroleum manpower are likely to be specific petroleum institutes and Unesco is in agreement with the United Nations Special Fund in envisaging the creation of such institutions in an additional number of developing countries.

UNESCO's special scientific institutes have in the past ranged over a wide variety of fields. They have been on the national level, on the regional level and on the international level. Just to mention some of the national institutes and specialized laboratories, UNESCO has been concerned with the building up of specialist training in such different fields as chemical technology, metallurgy, computation and geo-physics, including seismology. On the regional level, centres have for instance been set up for pure and applied mathematics, for hydrology and artesian water studies, for basic and applied biology and for economics and statistics. On the international level UNESCO has - sometimes in partnership with other organizations - successfully organized the creation of such institutions as the Institute of Theoretical Physics; international museums of soil standards, various international seminars and many other ventures are now being taken under consideration. The success of all these institutions is showing the way to an equally successful promotion of special petroleum and petrochemical institutes within the framework of Unesco's activities.

At this moment we can refer to very detailed recommendations concerning technical and vocational education which were adopted by UNESCO's General Conference in December 1962. The programming of studies has been discussed by our Member States after very careful preparation of the secretariat, and we can base ourselves upon a very large body of previous general experience when approaching the education and training of skilled petroleum technicians and technologists.

According to these recommendations we shall always lay stress on the broad basis which must be laid for later specialization or advancement during the education and training of engineers and technologists. In addition to acquiring their specialist knowledge, UNESCO is determined that technicians, engineers and technologists should study the social and economic aspects of their respective fields, and their training programme will be set up so that they remain conversant with the continuing development of techniques of their speciality. The above-mentioned recommendations go so far as to include the study of one foreign language of world-wide use within the teaching programmes so that the student is cnabled to remain aware of the progress in the field of science in general as well as in his special field of instruction. This last feature is understandable in its importance, as translations are for the time being not yet frequent enough to allow a technologist constant contact with world progress in his field.

# IV. UNESCO'S PLANS FOR PETROLEUM INSTITUTES

Further details regarding curricula and detailed planning of UNESCO petroleum institutes will undoubtedly be of interest to all participants in these discussions but it is too early to give more than some general notes on what is being planned at UNESCO's Headquarters. We are, of course, co-ordinating our efforts very closely with those of other members of the United Nations family, and we are making every effort to correlate our ideas with those of the trained personnel of the Special Fund and of the United Nations Commission for Industrial Development.

Some chemicals are manufactured on the basis of imported petroleum derivatives as raw materials: this is for instance the case of ammonia and nitrogenous fertilizer plants transforming imported bunker fuel into finished simple or multiple plant nutrients. However, in the case of normal developments, petrochemicals are made in connexion with and geographically close to a refinery of crude petroleum --- most frequently even in industrially advanced countries. In turn, petroleum producers are more and more frequently insisting on converting some of their refinery products into organic chemicals, as the prices obtained for fuels and nonsynthetic lubricants are more frequently considerably lower than the ton-per-ton prices of the chemicals and further conversion products which can be obtained from simple refinery deriva ves.

If industrial and scientific progress continues at the rapid pace of the last two decades, it is quite possible that petrochemicals will outweigh ordinary petroleum products in the not-too-distant future — at that time, of course, the emphasis in training institutes will also shift more toward petrochemistry and away from oilfield and petroleum production techniques. However, even at that time there will probably exist no need to separate petrochemical from general petroleum institutes for scientific and technological training and research in the then remaining developing countries.

Local needs are in every case the main consideration determining the specific aspects of any institute in petroleum and petrochemical technology which must be shaped according to the national level of general technical instruction available before the petroleum institute has been planned. To be specific, if sufficient geologists are being trained in a country, it will be unnecessary for a petroleum institute to offer detailed courses in geology. It is not warranted to spend any of the naturally limited resources on duplicating in a developing country instruction which is already sufficiently detailed also for petroleum and petrochemical needs. A petroleum institute must offer facilities for all those specific techniques which no other industry requires. On the other hand there are many graduates of other engineering schools active in the petroleum and petrochemical industries who have not had much special additional training.

For technologists it is altogether post-graduate training of engineers which seems best to fill the existing requirements. One to one-and-a-half years of specialized training can normally transform a mechanical, civil or chemical engineer into a petroleum engineer who is immediately useful in the field. A man with a bachelor's degree in a science of related nature, for instance a physicist or a chemist, is ideally suited to be a student of a petroleum institute. Equally, an engineering student, even if he has completed only two-thirds of his engineering training at another school, may be sufficiently pretrained to be successfully instructed at these specific petroleum schools which we are now planning. The technologists will get training in subjects which specialists with long experience have selected and approved, and it is planned to make sure in every case that the Government officers in charge of or supervising the locally active industries are fully satisfied with the planning and progress of petroleum training which is carried out in their country. More than in many other industries, the people in the actual production must be considered as the best judges with reference to the details of all instruction to be given, as they are best qualified to assess the specific manpower needs of a given area.

Regarding high-level technicians the task is somewhat similar. The tasks of the trained men needed everywhere as specialised craftsmen, testers, drillers, refinery operators and chemical plant specialists are today internationally quite uniform. It is possible to draw on previous experience in many countries and also on established training literature when instructing the right men with necessary pre-training skills in the specific needs they will encounter when working as petroleum technicians. As mentioned before, all-round training will be the aim, with specific attention to the hazards of the raw material. There will be climatic differences to be considered according to the location of the petroleum institutes and, for instance, in Argentina the trainees will be of a very different calibre from those we are likely to encounter in a Middle-Eastern country. But as the raw material is the same on a globe-wide basis, it is likely that the particular aspects of technicians' training in petroleum institutes will soon be widely generalised and satisfactorarily accomplished according to establlshed norms.

Great emphasis must be laid on new techniques and up-to-date modern equipment and its usage: the petroleum institutes, in addition to their training facilities, must be equipped with research laboratories where every new venture in technological progress can be independently checked and possibly tried out under

loce) conditions We believe that it is essential to aveid obsolete techniques and to be in every single area in possession of the latest technological knowledge so that production of petrochemicals and also of petroleum and its derivatives can be carried out on a profitable basis according to international standards. As the world petroleum industry is relatively young and as new techniques are still constantly being developed, it would be dangerous to rely on relatively old-fashioned equipment and possibly to condemn the developing countries to use techniques which no advanced country would consider any more as economical. This point is of specific significance for petrochemicals where a constant flow of new patents and processes continues to upset the established routine manufacturing processes. Not only fuels and lubricants, but also elastomers, synthetic fibres and plastic materials in general are continuing to show revolutionary progress because cheaper and better methods are invented, thereby obsoleting previously acceptable standards. The petroleum institutes which are being created by UNESCO must have facilities and personnel, which enable the workers in a particular country at least to follow world progress in their field, even if they are not immediately called to develop new techniques of their own.

On the other hand, they must be well enough equipped and trained to use local raw materials and local conditions to optimum perfection. The quality of the products must be constantly improved and the productivity of the industry should be permanently checked, so that the petroleum institute can lead the national activity in this field and make it profitable and competitive. It will be important that in some tropical countries specific attention is given to deterioration by moisture and permanently high humidity with reference to all equipment as well as to the products and intermediates. Again, such questions as the gas pressure in the fields which differs from place to place must be locally analysed and the best use must be made of all available techniques so that productivity is at the attainable peak at all times and that the resurves are being economically exploited and not prematurely exhausted. Many examples come to mind of how a petroleum institute can assist the national industry and make sure that all scientific and technological progress on a world-wide basis is immediately made useful for the local activities.

It might also be mentioned that the petroleum institutes will have many auxiliary functions which are not immediately connected with the specific knowledge of petroleum people. They will have to obtain and scan the necessary documentation and to provide a constant flow of information so that every man in the field can draw on the accumulated knowledge of the world's petroleum industries with as little delay as possible. Reference material, particularly also geological, drilling and production samples, must be organised in an usable fashion. The petroleum institutes will also have to check on the best ways of co-ordination of all efforts: economic considerations and statistical surveys will come within the range of their activities. They will also be concerned with questions of health and hygiene with reference to the workers in the field, and altogether the social

aspects of the work in the petroleum and petrochemical industries must not be overlooked in the programming of petroleum institutes. UNESCO can usefully compare these institutes with other centres which have been created and successfully operated on the basis of long years of experience.

The auxiliary work, besides strictly technical education, of both technicians and technologists must most probably also contain instruction in some bookkeeping techniques. It will be important that all graduates from petroleum institutes are able to draw up and also to analyse data referring to observations of instruments of all kinds, and statistical tabulations as well as elementary mathematics connected therewith must form a subject of study. Or course, instrumentation must altogether play an increasingly important part in petroleum and petrochemical training. Automation is indispensable in most chemical plants of today and familiarity with instrumentation and its problems is often a main guarantee for satisfactory performance of petroleum technicians. For technologists, report-writing is another subject not to be overlooked in general training.

Furthermore, on-the-job training must be co-ordinated with the formal scholastic training at the petroleum institutes. Local conditions will again vary, but in all cases it must be foreseen that the distance between the petroleum institute and the actual places of production is not too great, so that the trainces can check their theoretical knowledge against field conditions, even while they are at the institute. This feature will be more important for technologists than for technicians. A petroleum refinery or an oilfield car immediately be better understood when a traince gets to see the actual performance while he is mainly occupied with book-learning and theoretical courses. It is planned to take into account all aspects of petroleum techniques and petrochemistry when planning a certain amount of field training during the training at the institute.

For petrochemical training, trainces should have frequent occasions to see the actual plants in operation, to assist during shift-work and to visit the control laboratories where both the input and the output of the plant is being currently checked. For petroleum technologists, it will be necessary to get acquainted at an early stage of their training with the different aspects of field work which they will encounter after they have received their diploma. The aspects of exploration and drilling can be visualized during field trips and prolonged stays with the crews in the field. Pipeline work should preferably include inspection of existing pipelines as well as of lines in the process of construction. Work including tank-trucks, tankers and distribution stations should not be overlooked during training. Finally, laboratory work at the institute will parallel testing in actual production laboratories, but it would be important to have trainees acquainted with the actual routine testing and controls as they occur in production work.

For technicians, all these features of their training will become realistic after they have received their school training. On the other hand, technologists may frequently have no further occasion to get acquainted with these aspects of petroleum and petrochemical work which they must know at least in outline, before they can assume their specialized duties.

# V. LEGISLATIVE AND FINANCIAL ASPECTS OF MANPOWER TRAINING IN DEVELOPING COUNTRIES

In many nations there are specific government bodies concerned with scientific and technological questions: existing research councils must be consulted and represented within the supervisory structure of institutes and other scientific or technological endeavour.

In every case, it will be a question of suitable co-ordination of UNESCO plans with those of the local authorities through the customary or established channels: an independent UNESCO activity can never be planned according to pre-set patterns unless it is exactly corresponding to local desires and plans. The various existing UNESCO institutes are, in every case, ruled in their functioning by the wishes of the local authorities.

In every case it is of course planned to make training facilities large enough so that some space remains open where nationals from neighbouring countries could be trained at the same time as local nationals. However, the requests which are at present being processed by UNESCO come mainly from populous states desirors to create national petroleum institutes. At a later date, after several of these institutes have started functioning, it may be the logical next step to enlarge them so that they can also serve nationals of one or several neighbouring countries rather than to end up with one petroleum institute per country within a relatively small geographical region.

With regard to all manpower training, also in the field of petroleum and petrochemistry, we are concerned with long-range planning and humanitarian aspects, and less with questions of economical short-term importance. Petrochemistry is bound to play an important part in local developments for a very long time to come, even if the energy aspects of the petroleum industry may change to a considerable extent because of the availability of cheaper energy from other sources, for instance from atomic power. No other chemical raw materials are likely to replace the various raw material streams now derived from petroleum refining and natural gas processing. It is also for this reason that long-term planning including conservation of this raw material is of such vital importance for humanity.

The UNESCO General Conference, held at our Paris Headquarters, has been deliberating on a new division of efforts between two special departments of which one is devoted to the advancement of science, the other to the application of science and technology to development. The new arrangements will put a more definite emphasis on the practical needs for engineers and other technical personnel. The Geneva Conference of 1962 (UNCSAT — United Nations Conference on the Application of Science and Technology for the Benefit of the less developed Areas) which was organised by the United Nations, but also strongly concerned with UNESCO work in the developing countries, outlined in many fields how technology in addition to pure science can be brought to bear on progress in the countries under development which cannot immediately draw on their own scientific institutions. It is not planned to cut down in any way on the purely scientific efforts for which UNESCO has been responsible in the past and which will be further emphasised particularly on a regional and international basis within the proposals of our new bi-annual budget for 1965-66. On the other hand, additional posts under an additional director have been created so that the application of science can be furthered and the developing nations served even more effectively by the UNESCO Secretariat.

### VI. FUTURE OUTLOOK

UNESCO's emphasis has always been on the practicability of our endeavours to improve living standards of all human beings through a multi-national effort. In addition to the many successful ventures for which UNESCO has been responsible, there are, of course, many goals talling within the general area of our activities. Because of our past performance, we have been permitted to work with considerable amounts of capital at the disposal of the Special Fund of the United Nations and of the Expanded Programmes for Technical Assistance, and we expect to be further entrusted with many new projects which will involve large investments to assist governments intending to create new petroleum industries within the borders of their countries.

Regional conferences are at this time planned for various parts of the globe where super-national efforts may benefit individual countries. The "UNCSAT" agenda of 1962 was too wide in its scope to permit early practical solutions of regional problems, and a first Latin American regional conference is at present being prepared by UNESCO in co-sponsorship with the Economic Commission of the United Nations for Latin America, where the Latin American continent will be specifically considered in connection with the application of science and technology to less developed areas. After this first regional conference, others may follow, but we are of course depending on the course of world events in connection with our long-range planning. The petroleum and petrochemical developments depend upon the interplay of world demand and world prices: while individual countries may in the beginning see no hindrance or possible negative aspects when they engage in petroleum and petrochemical developments, it will not be long before

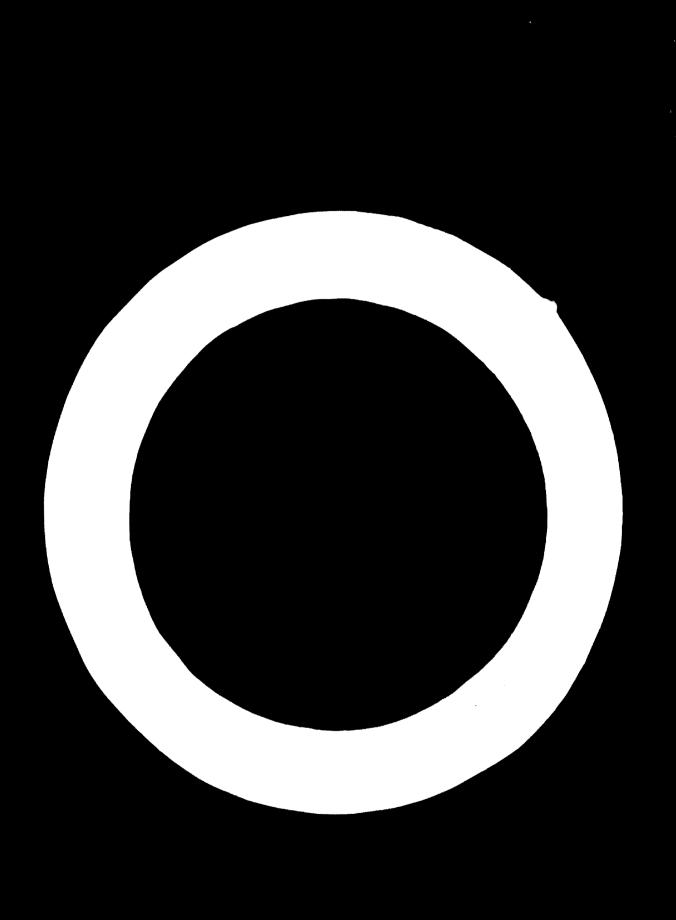
some attempts of world-wide co-ordination become essential. The manufacture of such products as synthetic fibres, fertilisers, industrial gases or plastic raw materials in any single country will be strongly determined by the world supply of these particular commodities no national planning can succeed without regard to regional and world economics, in tuin, an over-expansion of a particular industry could be disastrous for a national economy.

This in turn, of course, influences manpower planning. There exists a permanent interest of all governments to avoid redundancy of highly trained technical personnel which cannot find an outlet for their skills. With regard to manpower for petroleum and petrochemicals, we are of course, far away from the day when we have too many trained people anywhere in the developing countries. Training facilities must eventually be co-ordinated according to world-wide educational nords and it will again be beneficial for all Member States if UNESCO's international staff can draw upon its experience in all planning and programming of manpower aspects.

The critical future of our world economy is caused by the rapidly increasing world population confronted with a limited amount of natural resources. Regarding the availability of institutes of training, the globe is at present very irregularly endowed with universities and higher training institutes. A recent UNESCO estimate arrives at the conclusion that on an average one million of population require one university or one higher training institute. This means that the developing world of Asia. Africa and Latin America requires several hundred universities or higher training institutes but UNESCO can only envisage the creation of these training facilities during a period of some twenty-five or thirty years. In terms of scientists, engineers and other highly qualified technical personnel, our most recent figures indicate that the same three regions with approximately one thousand million people do require as many as five million highly trained specialists in the fields of science, engincoring and technology, and this figure is a rather concervative one, while the optimum figure could possibly be twice as high. Looking at the manpower needs of the petroleum and petrochemical industries, there also remains ample scope for very careful planning so that the global requirements are filled within the shortest possible time. It is UNESCO's firm determination to participate to the best of its ability in this challenging taak.

Chapter IV

# INDUSTRY STUDIES



# A. Raw materials and basic intermediates

# INTRODUCTORY SUMMARY

Since the Second World War, there has been a phenomenal increase in the utilization of raw materials of petroleum origin to provide the basic building blocks for the manufacture of those commodities which are now classified as "petrochemicals". These raw materials are transformed by stages into the more familiar end-use products. First, they are processed into "basic intermediates", and then, often, through "secondary intermediates" into the end-use products.

The raw materials for petrochemical products are classifield according to their stage of transformation through various technical processes towards the final product as follows:

(a) Raw materials:

Petroleum and natural gas.

(b) Basic intermediates:

These include the hydrocarbons of olefins, paraffins and aromatics, namely: ethylene, propylene, butylene, methane series, benzene, toulene, xylenes etc. The methane group of hydrocarbons occur in both crude oil and natural gas. Refineries provide hydrocarbon gases and liquids. Acetylene and butadiene, which may be by-products of olefin manufacture, belong here as well.

(c) Secondary intermediates:

These include *inter-alia*, the basic intermediates which have been processed into the following: aceta dehyde, acetone, styrene, polymers, caprolactam, acetic anhydride, vinyl chloride, methanol, ammonia, glycol, polyisobutylene, alcohols, and polyolefins.

(d) Final or end-use products:

These include plastics, synthetic fibres, detergents, nitrogenous fertilizers, synthetic rubbers, automotive chemicals, resins, insecticides etc.

In the production of petrochemical commodities, the intermediate raw materials are often either competitive or complementary. For example, olefins might be used in place of acetylene as the building block for the petrochemical industry. Such end-use commodities as vinyl chloride monomer, vinyl acetate monomer, acrylonitrile, trichlorethylene, can be based either on acetylene or ethylene and propylene. In the United States of America, ethylene costs an average of  $3 \notin per lb$ . as a basic intermediate for chemical synthesis. But acetylene costs  $10 \notin -12 \notin$ , hence ethylene appears to be the less expensive starting-point for the chemical industry. But it is suggested that if improved processes can be developed so that a 100 per cent conversion of a hydrocarbon into acetylene becomes feasible, then its cost will decline markedly and acetylene might form the basis for a petrochemical industry in developing countries where refinery by-products are meagre. The optimum choice of raw-material base will, therefore, depend on relative costs.

In the petrochemical industry, one finds not only competition or complementarities between the basic intermediates as raw materials but also between processes". It is a peculiar feature of this industry that its production functions, defined for given raw materials, admit a relatively high degree of substitution between processes for given qualities of outputs. This means that there are always several different ways of producing the same petrochemical commodity. For example, olefins can be manufactured in different ways, namely, by continuous cracking in tubes with external heating or, by continuous cracking on fluidized mass or, by cyclic cracking. A study of the basic raw materials should, therefore, proceed part passu with the study of the technologies involved in their transformation, with a view to finding the optimum processes for utilization of the raw materials - bearing in mind not only the main product but also the by-product that might be generated, i.e. if acetylene is chosen as the basic building block, should it come from carbide, natural gas, or petroleum distillates ? If ethylene is chosen instead, should it come from naphtha cracking as in Japan or be based on refinery-off gas as in the United States ? The optimum choice of intermediates and processes will, of course, depend on the quality of the basic raw materials locally available, opportunity costs, and - in the case of processes - on the value assigned to the hy-products that will be generated.

# **1. THE PETROCHEMICAL INDUSTRIES**

# Prepared for the United Nations Centre for Industrial Development by l'Institut français du pétrole

# I. General conditions and main petrochemical routes

more and more delicate operations, closer and closer implantations from consumption markets.

The inventory of present or potential availabilities in raw material offers, generally, all possibilities for a development in the petrochemical industry for the countries having petroleum or natural gas sources.

These possibilities are numerous and their relative importance is very different. Figures I and II show the main petrochemical routes which lead from natural gas or petroleum to the great intermediates and end-products.

These different routes lead to: more and more elaborated products, which require higher and higher investments, Some of these routes are rapidly becoming obsolete and those processes which lead to too high an operating cost are abandoned for the benefit of utilizing new routes which by-pass the intermediate stages of production.

According to these elements, and to meet the economical imperatives connected with the selling price of products on the internal or export markets, it is of first importance that the developing countries wishing to realize a petrochemical industry, should choose the most economical routes and the most suitable processes

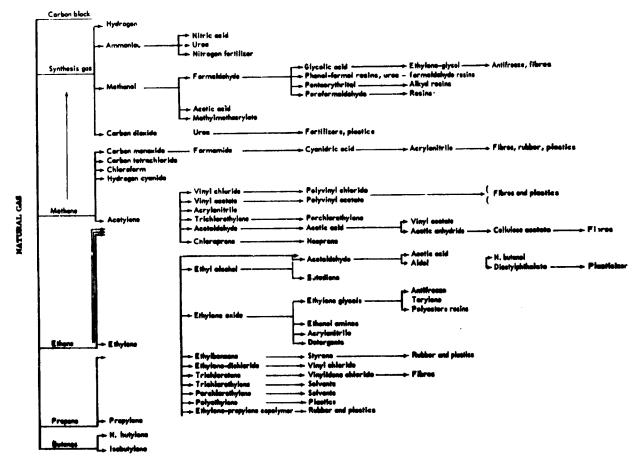


Figure I. Petrochemicals manufactured from natural gas: main petrochemical restar

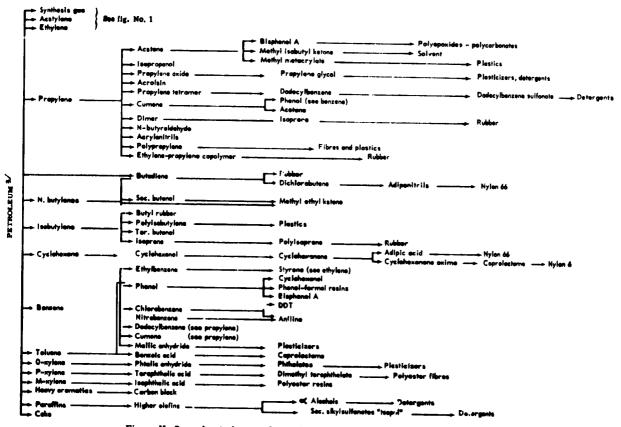


Figure II. Petrochemicals manufactured from petroleum: main petrochemical routes

and consequently that they should settle their industry starting from a raw material chosen according to the above-mentioned factors and to the conditions discussed in the first section of this study.

# II. Definitions and importance of the main products

A petrochemical product is a product issued entirely or in the most part from petroleum or natural gas sources. Petrochemical products are mainly aliphatic, aromatic, or naphthenic compounds and their derivatives, but they can be inorganic such as sulfur, ammonia and carbon black. The range of petrochemical products includes:

# Basic products of first-generation petrochemicals

Aside from carbon-black, this group includes hydrogen, synthesis gas and those purified hydrocarbons which are formed in economically recoverable quantity in the course of petroleum-refining operations. It is also customary to include, among the first-generation petrochemicals: acetylcne, ammonia and methanol, although neither of these compounds can be recovered directly from refinery streams. Ethyl-bennens, on the other hand, which is being recovered on a very large scale from C<sub>0</sub>-arcementic reformate by super-fractionation, Intermediate and end-products or second-generation petrochemicals

is usually considered a second-generation petrochemi-

cal because the bulk of its output stems from the

On the other hand, quantities of first-generation petrochemicals which can be recovered from refinery streams are not always sufficient to satisfy market demand.

Some of these commodities are therefore synthesized in large volumes as main products. This is especially true of ethylene, butylene, butadiene and benzene.

alkylation of benzene.

Chemical conversion of the basic products leads to the second generation of organic chemical intermediates. At this step, we come to the first group of products which have significant end-markets without further chemical conversion: polyolefines, chlorinated solvents, alcohol etc. In most instances, however, a second and even a third or fourth chemical conversion is needed to reach the form required by the end-user. Strictly speaking, ethylene glycol which comes from ethylene oxide conversion is a third-generation derivative of petroleum. Nevertheless, it has become the custom to include among the second-generation petrochemicals the entire large group of intermediates and end-products derived from petroleum stocks, i.e. the group which finds its main outlet in one of the five functional TABLE 1

	1962 Production ( (me)	Selling price (SUS/ton)	Value / MM &US
Ethylene	2,800,000	100	280
Ethylene oxide	690,000	340	234
Ethyl alcohol.	830,000	200	166
Styrene	820,000	220	180
Polycthylene	860,000	400	344
Propylene	1,330,000	54	72
Isopropyl alcohol.	500,000	150	75
Cumene	250,000	220	55
Acetone	400,000	130	52
<b>Pheno1</b>	390,000	240	94
Acetylene	360,000	240	86
Vinyl chloride (from acety-			
lene)	120,000	180	22
Butadiene	900,000	240	216
Benzene	1,850,000	60	111
Styrene-butadiene rubber	1,435,000	470	675
Ammonia	5,200,000	60	312

applications: solvents and plasticizers, plastics and resins, synthetic rubbers, fibres and miscellaneous products as surfactants, detergents etc.

The importance of certain petrochemical products of great consumption is shown in table 1 where the values of the main productions are calculated for the United States of America (yearly tonnage multiplied by the possible selling price on the market).

# III. Present and future trends of petrochemical production

With the bulk of petrochemical output consumed in further industrial conversion, the prospects of individual petrochemical products are controlled by the customer industries' outlook.

A recent analysis<sup>1</sup> traces this relationship between the prospects of individual end-use groups and the growth potential of ethylene as follows :

Bed unv		Percentage of total substance proves					
		1966-79	1959-60				
<b>Plantin.</b>		63.4	43.2				
Selvents		6.9	5.8				
Hinstomers		5.8	17				
Detergente		4.2	4.8				
Anti-freeze		2.9	13.4				
Synthetic fibres		1.5	1.2				
Anti-knock Suids			3.5				
Misselfancous	•	15.3	22.0				
		100.0	100.0				

<sup>1</sup> Industrial Chamier (http://bith.

However, even these outlets are still intermediate industries, the consumer markets which control are still one or two generations further removed, and here we may attempt a breakdown of demand categories in the following major end-product lines consuming petrochemical intermediates: plastics, surface coatings, synthetic fibres, synthetic elastomers, detergents, automotive products, and fertilizers.

## III.I. PLASTICS

In the highly diversified field of | lastics, the big identifiable end-use markets are: construction and packaging. Other final markets for plastics are of a different order of magnitude — motor-cars, footwear, toys, and boats.

A reliable breakdown available for synthetic resin production for the United States of America is given hereunder for 1962.

Product group	Percentage US production
Polyolatines.	28
Vizyls and vizyls copolymers	21
Polystyrenes (incl. copolymers)	16
Phenolics	8
Alkyde	7
Aminoplastics.	7
Other (acrylics, polyesters, expenses)	13
	100

It should be noted that these figures include resins consumed in surface coatings and adhesives.

In terms of growth rate, the polyolefines are the best performers. High-pressure polyothylene has grown at an average annual rate of 22 per cent since 1955. Low pressure polyothylene has finally come into its own as domestic consumption increased at a rate of 33 per cent from 1962 to 1963. For polypropylene United States consumption is expected to grow at an annual rate of 30-40 per cent through 1964.

The second-largest plastics family, vinyls, is also the second best performer in rate of growth. Its United States consumption expanded by 20 per cent in 1962, with main growth shown in floor coverings, coatings and moulded products.

The annual rate of growth for styrene resins is currently about 12 per cent The other three major categories : phenolics, aminoplastics, and alkyds have, in general, settled down to slow-growth trends (3-4 per cent per year).

In Europe, the rate of growth for plastics is about 10 to 15 per cent with the best performance for polyethylenes.

#### III.2. Symmetric Plana

Among man-mode fibres, we distinguish the groups of glass fibres, sollulosics (rayon and acousts) and the wholy synthetics.

The first named enterpary is not a significant petrochemical market : production of adhesian looks into

the petrochemical industry for its supply of acetic acid, acetic anhydride and some of its carbon disulphide. However the long-range trend of cellulosics is unfavourable. United States production in 1962 was still below the 1958 output.

The brightest outlook is in the field of wholly synthetic fibres where three main chemical groups are involved.

(a) Polyamide fibres (nylons), which call, above all, for adipic acid, adiponitrile, hexamethylene diamine and caprolactam as raw material;

(b) Polyesters which consume dimethyl-terepthalate, along with some ethylene-glycol;

(c) The acrylics which draw on acrylonitrile along with some vinyl chloride and vinylidene chloride.

The brightest growth prospects are in the nylon field, but the acrylics and the polyesters are developing so in the United States, Nylon 6 (based on caprolactam) has only 12-14 per cent of the nylon market although it predominates in Europe, and the acrylics production is brighter than the polyesters production, although polyesters predominate in Europe.

#### III.3. SYNTHETIC RUBBER

The world demand for rubber has been increasing very rapidly and is now about 4.9 million long tons per year including that produced within the Soviet bloc.

End-uses currently have approximately the following distribution:

		Per sent
Tyre and tyre products		63.0
Mechanical goods		13.0
Shoe products.		5.2
Later from pro- unin	• •	3.8
Wire and cable costings	• •	1.5
Adhesives		1.5
Other	•	12.0

108.0

World production of natural rubber is presently about 2 million tons per year or less than 50 per cent of the total requirements. By 1970, the total world demand for rubber is expected to reach 6.4 million tons, while natural rubber production will be expanded to only about 2.7 million tons. The balance of world rubber requirements must necessarily be supplied by synthetics.

In the US, an important development in the production of SBR which still is in overcapacity, is not foreseen, neither of Butyl which is limited in its utilisations.

The most important development will come from new sterecepscific rebbers: polyisoprens, polybutadiens and copolymer of ethylene and propylens. The new polymers can be substituted for natural rebber in most of those applications where SBR cannot serve as suitable substitute.

In Europe and USSR, the situation is quite different, the SBR market is developing very quickly, and the butadiene domand will be very high in the coming years. It is the same for stereospecifics: polybutadiene and polyisoprene, called to a great development in the next years.

The Asian countries, and generally the developing countries, offer some market caracteristics similar to those in USSR.

## 111.4. DETERGENTS

It is estimated that 75-80 per cent of the total demand is for household detergents. The remaining 20-25 per cent enter into the industrial detergent's market in a wide variety of industrial applications.

Household detergents are mostly based on alkyl aryl sulphonates, fatty alcohol sulphates plus some nonionics.

In the anionics market alkyl arylsulphonates are predominant, accounting for 45 per cent of the total. The main growth in detergents is presently in the nonionics and in the liquid anionics formulations.

## III.5. AUTOMOTIVE CHEMICALS

Among additives for petroleum products, anti-knock compounds (TEL, TML, etc.) are the biggest factor. Ethyl-chloride and methyl chloride are the intermediates used in their manufacture.

Ethylene glycol, used as anti-freeze has been a rapidly rising petrochemical throughout the 1950's and in 1962 served 92 per cent of the total anti-freeze market. Promising for glycol is also the market of polyester fibres and films.

## III.6. AMMONIA AND FERTILIZERS

Rapidly expanding world demand for nitrogen fertilizers and technical nitrogen products is reflected in the large number of new plant projects. These have been prompted as much by the real or potential demand in developing countries, as by the increasing fertilizer requirements in industrially developed countries and between 1957/58 and 1962/63 world N-capacity has increased by 6.3 millions tons N.

The domands occurring in 1963/64 have exceeded all forecasts, especially from China and other Asian markets. The result was an expansion of the European and Japanese exports to these countries where domestic production has not been advanced at a sufficiently rapid rate to meet expanding domand.

It is estimated that the nitrogen production during 1963/64 will reach 16.5 million tons or 6 per cent more than in 1962/63.

An important feature has been the emergence of new exporting countries which, in previous years, have been traditional markets. Countries such as Portugal, Pakietan, China, Trinidad and South Africa have started to export nitrogen materials on an increasing scale and, as other new projects are completed, more countries and territeries such as Colombia, Venezuela, Aruba, Greece, Kuwait and Iran, can be expected to achieve exportable surpluses.

18.17

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## IV. Basic products or first-generation potrochemicals

These products are at the start of the manufacture of the main petrochemical intermediates and can be manufactured from various petroleum raw materials.

Their importance is different as well for the produced tonnage as for the price level. An idea of that importance can be obtained by regarding table 1.

Ammonia is the first one, for the produced tonnage as well as for the turnover.

Ethylene and butadiene come, respectively, in second and third position (because of the high price of butadiene)

Benzene, acetylene and propylene follow.

If prices are taken into account: butadiene and acetylene are expensive products (high operating cost); ammonia, ethylene, benzene have intermediate prices; propylene, considered as a by-product of the ethylene production, is relatively cheap.

In the following discussion, we shall be concerned with production of the following principal chemical feedstocks: lower olefins as ethylene or propylene, acetylene, diolefins as butadiene,<sup>a</sup> aromatics as benzene and xylenes, ammonia and methanol, carbon black and sulfur.

The study of the different productions will be based on

- The investments and the variation of the manufacturing cost and the selling price of the products with the capacity of the plants;
- The comparison of the different processes and the competitive petrochemical routes.

The operating cost elements will be furnished for all productions considered and the influence of the variation of these elements between the industrialized countries and the developing countries will be shown for some standard examples, taking into consideration: different modes of payment and financing of the installations; different costs of construction, manpower, chemical products and catalysts; price of raw materials and utilities suitable to the various countries.

In order to accomplish this comparison we will use the standard calculation method described previously and we will take as basic data the following hypotheses which are likely to be accepted in most cases for:

1. Industrialized countries:

Paymont of the plant: cash;

Depreciation at: 12.5 per cent of investment;

Pinancial charges (average) at: 3.5 per cont of investment;

Return on invostment <sup>a</sup> at: 20 per cent of investment; Taxes on the benefits at: 50 per cent of investment, 2. Developing countries:

Payment of the plant:

Financing for 2/3 of the investment by:

- Short-term ioan (5 years) at 8 per cent compound interest, corresponding to 1/3 of total investment;
- Long-term loan (10 years) at 8 per cent compound interest, corresponding to 1/3 of total investment.

Equity capital for 1/3 of total investment;

Depreciation at: 12.5 per cent of equity capital; Financial charges (average) at : 3.5 per cent of equity capital;

Recurn on investment<sup>a</sup> at: 20 per cent of equity capital;

Taxes on the benefits at: 50 per cent of equity capital.

If the studies based on such hypotheses can lead to cost prices and afterwards to sales prices, it should be remarked nevertheless that the results obtained can only be considered as typical examples valuable in the scope of such conditions. It is therefore necessary for any future petrochemical plant well defined to evaluate accurately the specific elements of the project and the economic factors applicable for the country where the plant will be erected, in order to carry out, by uring the methods analysed in this report, the economic study of the project under such conditions.

IV.1. THE INDUSTRIAL PRODUCTION OF LOWER OLEFINS

#### IV.1.1. INTRODUCTION

A considerable part of the heavy organic chemicals industry is based on lower olefins such as: ethylene and propylene, produced by cracking of petroleum feedstocks.

These two simple olefins, manufactured to-day on an enormous scale, are the basic building blocks for a large proportion of the aliphatic organic chemical production.

#### Ethylene

Contrary to USA practice, where ethylene production has been based primarily on redinery off-gases, LPG and ethane separated from natural gas, ethylene production in Europe and Japan has been based primarily on the pyrolysis of naphtha. As a general rule, the pyrolysis of naphtha in the USA only occurs where there is a demand for the other olefins produced; however, in Europe and Japan, naphtha is cracked primarily because it is an over-supply, chanp and easy to ship.

Small quantities of ethylene are extracted from coke oven gases; countries such as India produce ethylene from dehydrolysis of fermentation ethanol, France obtains some ethylene requirements by cracking ethane separated from Lacq natural gas and refinery streams are utilized where available.

<sup>&</sup>lt;sup>9</sup> Inspress will be studied with the intermediate products (see chapter V).

<sup>\*</sup> Beturn required for a fre-year papert.

Probably 80 per cent of ethylene production outside of the United States is based on naphtha, and this percentage should rise in the future.

Actual consumption of ethylene will continue its rapid growth, with polyethylene, styrene monomer and vinyl chloride being the most important markets. Ethylene is already replacing acctylene in Europe as a raw material for acetaldehyde and vinyl chloride production and this trend will continue.

Ethanol consumption will decrease; however, this will not affect ethylene markets, since the loss will be to the direct oxidation of ethylene to produce acetaldehyde, thus eliminating the ethanol step.

The future of ethylene is keyed to plastics: polyethylene, polystyrene and polyvinyl chloride and elastomers: EPT rubbers. These derivatives are being dealt with in other chapters (see Chapter V) of this volume and hence will not be considered here any further.

#### **Propylene**

In the US there are substantial quantities of propylene available from catalytic crackers at a purity of 40-60 per cent, which is satisfactory for isopropanol, propylene oxide, acrylonitrile and tetramer production. Propylene is also co-produced with ethylene during the cracking of LPG's.

For newer uses, propylene purity requirements are more severe (90-95 per cent required) and in the case of polypropylene, purity should be at least 99 per cent.

The propylene situation outside the United States is different. In Europe and Japan, where cracking facilities are not as extensive, refinery propylene is less available. However, co-product propylene production based on the cracking of naphtha is significant and it is expected that markets will have to be found for propylene: its use as a feed-stock for refinery alkylation and refinery polymerization processes is not as important outside the United States.

Primary growth markets are: EPT rubbers, acrylonitrile, polypropylene and propylene oxide. New potential markets include acrolein, butanols and isoprene. Propylene will gradually close its propylene tetramer markets because of the shift to biodegradable detergents.

In the production of ethylene from light naphtha and LPG's, propylene, butylenes, butadiene and arornatics are produced to varying degrees as by-products. In the naphtha steam-cracking especially, with the possible exception of butadiene, most of the chemicals obtainable as by-products are presently produced well in excess of demand. This justifies the use of lower or gross by-product values, e.g. fuel, LPG, motor gasoline, inasmuch as any upgrading or purification facilities must be justified on a basis of low "raw material values". Therefore, in general, the economics of ethylene production by naphtha pyrolysis are such that no allocation of manufacturing costs are assessed against the ethylene product.

By-product credits can only be taken as justified by internal requirements and/or markets for disposal. With the introduction of propylene derivatives such as : EPT rubbers, acrylonitrile, polypropylene and other endproducts in demand, and with the growth of butadiene demand, by-product recovery from naphtha pyrolysis plant and on a small scale from LPG steam-cracking, will assume increasing importance, with the value assigned to these by-products proportionally affecting the production economics of ethylene.

# IV.1.2. ECONOMICS OF OLEFINS PRODUCTION

# IV.1.2.A. Factors considered

In examining the economics of ethylene production from LPG's and light naphtha, four main factors stand out as having important effects on costs. These are the following:

# 1. Raw materials availability and prices

Some 40 per cent of current United States production is based on refinery gases (both direct recovery and conversion of ethane and propane); 45 per cent is derived from cracking of propane and ethane recovered from natural gas. Most of the remainder draws on liquid hydrocarbons as feedstock.

In recent years there has been a pronounced growth trend in the role of such liquid feedstocks, especially in Europe and Japan, where there is an overabundance of light naphtha fractions (it is assumed that this abundance may be attributed to the present difficulty of disposing of it or upgrading it to high-octane motor gasoline). However, in the United States too, light naphtha now serves as feedstock at major ethylene plants. A major attraction is the formation of a highly aromatic liquid by-product in the gasoline range, which bears some of the manufacturing cost by reason of its high blending value. Several hydrogenation processes to stabilize these by-product fractions have recently become available.

The yield of ethylene depends on feedstock and can be adjusted to market requirements.

#### (a) Ethane pyrolysis

Moderate variation of the ethane pyrolysis conditions will not notably affect the ultimate yields. However, the variations in conversion rate will affect the quantity of ethane recycle, the furnace throughput, the quantity of gases to be compressed and the utilities consumed. A conversion rate of 60 per cent per pass has been selected as representative of good commercial practice. An ultimate ethylene yield exceeding 80 wt. per cent of the ethane feed is anticipated.

#### (b) Propane pyrolysis

Changes of propane conversion conditions would cause considerable variations in the propylene yield and the composition of the propylene-propane stream. However, the ethylene yield, based on converted propane, symains practically constant at higher conversion rates.

The following tabulation illustrates these variations of the yield pattern for three conversion rates:

Conversion per pass, percentage.	65.0	75.0	90.0
Approximate yield on propane charge, wt. percentage			
Residue gas.	24.0	26.4	28.2
Ethylene.	39.2	38.7	38.1
Ethane.	6.0	7.0	7.3
Propylenc .	29.0	23.3	14.9
Other hydrocarbons	1.8	4.5	11.5
Total	100.0	100.0	100.0
Ethylene yield after ethane cracking.	44.0	44.3	44.0
Total, charge to pyrolysis coils, wt. percentage on fresh feed	154.0	133.3	111.1
App. mole percentage propylene in propylene-propane stream	36.0	43.0	59.0

## (c) Naphtha pyrolysis

Naphtha composition affects ethylene and by-product yields which are attained at constant operating conditions of temperature, time and pressure. Dry gas yield varies from 62.6 to 69.0 wt. per cent, respectively, for paraffinic and naphthenic naphthas. This conversion range represents a good economic level for ethylene producers in the United States, although much lower conversion levels have been profitably employed in Europe. Predicted pyrolysis yields from three naphtha feeds based on relatively high severity operation are shown below:

Manhéa evase

		Napros Types	
Pyrotysis yields	Parafinic	hfid- continent	Naphthanic
Product yields, wt. percentage on feed			
H	0.9	0.8	0.9
СН	14.8	14.8	13.7
	28.1	25.2	24.2
C <sub>p</sub> H <sub>a</sub>	5.3	4.3	4.0
С.Н	19.4	18.7	19.3
С Н	0.5	0.6	0.5
TOTAL, dry gas	69.0	64.4	62.6
С.Н	2.5	3.6	3.8
<b>C.H.</b>	4.5	6.7	7.8
TOTAL C'S	7.0	10.3	11.6
Geselene	20.8	22.0	22.5
Puel ell.	3.2	3.3	3.3
TOTAL	100.0	100.0	100.0

#### Feedback values

Naphthas are readily available at a low cost as pyrolysis istocks in Europe and also in some developing countries to-day. They can be easily transported and

stored, if they are not available there where the petrochemical plant would be located.

In the United States, where naphtha is more expensive, it is less advantageous to use this raw material than in Europe. On the contrary, there are a great number of refineries which are big enough to be in a position to deliver 150,000-200,000 tons of ethylene per year, which is only based on refinery gas. Moreover, there are nearly unlimited quantities of ethane and propane available, resulting from stabilization operations and hence at much lower prices than in Europe. The prices of these various raw materials are presented in Section I of this study (see Chapter II.1.1.).

### 2. Product distribution

Individual producers of ethylene have different requirements for and set different values on by-products.

## TABLE 2. 80,000 TONS/YEAR STHYLENE PRODUCTION Unit 1. Naphtha steam-cracking

	\$US
Investment (grass roots plani)	
Process units Offsites including: general plant services; general buildings; utilities; receiving, shipping and storage	10,000,000
(land value is not included).	4,000,000 1,000,000
(land value is not included).	1,000,000
(land value is not included)	1,000,000

														-	-	-	
Tali gas.					•												45,000
Ethylene																	\$0,000
Propylene																	51,000
Butylene																	20,000
Gasoline																	57,000
Fuel oil																	9,000
Ethane re																	15.000
																	8,000
Loss .	•••	•••	•	•	•	• •	• •	• •	•	•	•	•	•	٠	•	•	e,000
Utilities req Fuel * (10													_	_	_		45
Steem (et																	25
Electricity	-		•		•												10.500
																	2,100
Cooling V																	50
Boiler fee		HET (		/ 88	<b>r</b> )	•	•	•	•••	•	٠	٠	•	٠	٠	٠	30
Catalyst an	d chi	mici	dr.	~	ųci	h			8								hg/day
Dessicent																	135
Caustic.																	1,900
Acetylene																	25
		~~	•	•	•	•	•	•	• •	•	•	•	•	•	•		

20 mm/shift

Taking into account fusi gas produced in the unit.

Pyrolysis gasoline, for example, may have considerable value to some, but can be used only as fuel by others. Product. distribution can be varied to the extent that flexibility is incorporated into the original plant design. A relatively small additional investment allows operation with alternative product distributions and with feedstocks other than light naphtha.

## 3. Plant size

The size of plant will naturally affect the manufacturing cost of ethylene. Plant size must be in economic balance with available investment capital, obsolescence, and future market potential, in order to establish the optimum plant capacity for individual situations.

# 4. Utilisation and value of by-products

These all influence the manufacturing cost of ethylene. Their effects on the economics of the plant will be presented hereafter.

# IV.1.2.B. Description of cases

In order to cover a wide range of typical feed-stocks and product distributions, economics for two types of steam-cracking have been evaluated. The two types of unit and the conditions which give rise to the differences in yield structure are as follows:

- Unit 1. A plant to produce 80,000 <sup>4</sup> tons/year of polymerization grade ethylene (99.0 per. cent) by high severity naphtha steamcracking with recycle of ethane product to pyrolysis;
- Unit 2. A plant to produce 80,000 tons/year of polymerization grade ethylene by steam-cracking of a feed charge composed essentially of ethane and propane.

# IV.1.2.C. Presentation of data

The investment, material balances, utilities, catalyst and chemicals requirements are presented in tables 2 and 3, for units 1 and 2, respectively, at 80,000 tons/year ethylene capacity.

A "base" economic evaluation is made assuming the following feed-stock, fuel and by-product values:

- Feed naphtha. An intermediate value of \$US 18/ton is selected for the base in this study (fucl value could be assumed at US\$ 15/ton and gasoline value could be assumed at \$US\$ 22/ton).
- Fuel. The value of fuel is at \$US 1.5/10<sup>6</sup> kcal, based on the current Caribbean and Middle-East fuel oil prices.
- $C_{\rm s}$  cut. The propylene-propane fraction produced as a by-product will contain approximately 92 wt. per cent propylene <sup>5</sup>; for "base" case the value of the  $C_{\rm s}$  cut is taken at LPG value \$U\$ 30/ton.

 TABLE 3. 80,000 TONS/YEAR ETHYLENE PRODUCTION

 Unit 2. Ethane and propane steam-cracking

OPERATING	COS	1	FLI	EMI	EN	rs				
Investment (grass roots plant)										<b>₩</b> US
UTTRICE (see table 2)										12,000,000
Start-up expenses	•	• •	·	·	•	•	•			1,000,000
		То	TA	L 1	N٧	/F.S	TN	1E!	T	13,000,000
Material Balances (with ethane	<b>8</b> 04	1,	<b>\</b> FO	na				~l	-)	Tonsiyear
Feedstocks		- ,		ha			,	, CP	c)	
Ethane Propane.									5,00 5,00	
<b>C</b> <sub>4</sub> +	•••			•			1		5,00 5,00	
Producta										165,000
Tail gas										40.001
Ethylene			•	·	•	·	٠	·	•	40,000
Propylene-propane						·	•	•	•	. <b>80,000</b> . 30,000
Butylenes-butadiene						:	·	•	•	4,500
Gasolene				Ż					•	4,000
					Ì		÷			1,500
Loss		•				•				5,000
Utilities requirements										-
Fuel * (10 <sup>s</sup> kcal/hr)										10
Second (export) (tota/m)										0
Electricity (kW/hr) Cooling water (included in e										4 660
Boiler feed water (m <sup>a</sup> /hr)						ur	np		) )	18
Catalyst and chemicals requireme							•	·	•••	10
Dessicant								1	7,80	0 kg/year
						•			480	tons/year
Acetylene catalyst	·	• •	•	•	٠	·		1	3,00	0 kg/yoar
Labour										
17 men/shift										

Taking into account fuel gas produced in the unit.

- $C_4$ 's cut. The  $C_4$ 's cut main potential lies in its butadiene<sup>4</sup> content; for base case, the value of the  $C_4$ 's cut is taken at LPG value \$US 30/ton.
- Steam-cracking gasoline. The gasoline product derived from light naphtha pyrolysis may require selective hydrogenation treatment to make it saleable. Taking into account this incremental treatment charge, the value of this gasoline having a clear Research ON of approximately 96, is taken at \$U\$ 22/tom.

In tables 4, 5, 6 and 7 the operating costs are given for the two units, and the corresponding selling prices of ethylene are derived.

<sup>&</sup>lt;sup>4</sup> This capacity has been chosen because of general tendency for building to-day larger steam-crackers which will be able to produce from 80,000 to 250,000 toms/year of ethylene.

<sup>\*</sup> Subsequent demand for end-products based on propyiese and butadiene feedstocks may increase its value accordingly (see IV.2.1.D).

# TABLE 4. 80,000 TONS/YEAR ETHYLENE PRODUCTION

Unit 1. Naphtha steam-cracking

Unde	Unit cost (\$US)	Annal qualitity	(10* \$	i cost (your)
MANUFACTUR	UNG COUT			
ariable costs				
Rew material				
Naphtha (tons)	18	285,000		5.1
Utilities				-,-
Fuei (10 <sup>e</sup> kcal)	1.5	360.000	540	
Steam (credit) (tons)	1.5	200.000	( 320)	
Electricity (10 <sup>e</sup> kW/hr)	10	84,000	840	
Cooling water (10 <sup>a</sup> m <sup>a</sup> )	6	16.800	100	
Boiler feed water (m <sup>3</sup> )	0.2	400,000	80	
			<u></u>	1,2
Catalyst and chemicals				
Dessicant (kg)	0.3	44,500	13	
Caustic (tons)	70	630	- 44	
Acetylene catalyst (kg)	4	8,250	33	
Patron and manufator				
Labour and supervision				
Salaries and wages (men/year)	5,000	80	490 160	
				9
TOTAL VARIABLE	COSTS			6,9
Ixed costs				
Depreciation				
Interest		at of investmen		
Maintenance		at of investmen		
		nt of investmen		
Taxes and insurance	i per ce	nt of investmen		
Тотац	PDOID COSTS			3,4
				-

# TABLE 5. 80,000 TONS/YEAR STRYLING PRODUCTION Unit 1. Naphtic steam-cracking

															_			 			 	
						8		L	NO													
Not each flow at 20 per	COL	<b>t</b> •	of	te	Hai		M				ł								•			3,000
Depreciation provides .					•	•																1,870
Plet income after laxes					•				•				•							•		1,130
Not income before taxee	at	50	pe	2 (		t	•	•			•	•		•			•					2,300
Manufacturing cost		•		•	•	•	•		•	•	•					•	•					30,430
Total sales					•							•							•	•'		

# TABLE 5 (continued)

	Annual cost (10 <sup>a</sup> §US/year)
by-product sales	
Propylene-propane         (51,000 tons/year at \$30/ton)         1,530           Butylene-butadiene         (20,000 tons/year at \$30/ton)         600           Gasoline         (57,000 tons/year at \$22/ton)         1,250           Fuel oil         (9,000 tons/year) at \$15/ton)         135	
TOTAL BY-PRODUCTS	3,515
thylene selling price (\$/ton)	9,125 114
	5.2

• Return required for a five-year payout.

# TABLE 6. 80,000 TONS/YEAR ETHYLENE PRODUCTION

Unit 2. Ethane and propane steam-cracking

Unit	Unit cont (BUS)	Annual quantity	Annual ( 10* \$/;	cest rear)
MANUFACTURE	NG COST			
Variable costs				
Raw material				
LPG (tons)	24	165.000		1.04
Utilities	•••	105,000		3,96
Bud (106 bast)				
Steam (credit) (tons)	1.5	80,000	120	
Electricity (10 <sup>e</sup> kW/br)	1.6 10	72,000	(	
Cooling water (incl. in electricity consump-	10	36,400	364	
tion)				
Boller food water (m <sup>a</sup> )	0.2			
	U.2	144,000	29	
Catalyst and chemicals				39
Dessicant (kg)				
Caustic (tons)	0.3	17,800	5	
Acetylene catalyst (kg)	70	480	35	
	•	13,000	52	
Labour and Supervision				9
Salaries and wages (men/year)	5.000	<b>62</b>	340	
Supervision (at 25 per cent of salaries and	-,	-		
wages)			85	
				425
	TOTAL	VARIABLE COSTS	-	4.871
ting and				
Tand costs Peperintien	2.5 per ces	t of investment		
Peperchaiten	12.5 per cen 3.5 per cen	t of investment		
Pepereision At 1 Interest	3.5 per cen 4 per cen	t of investment t of investment		
Pepervision At J Intervet At At Statements At At Contract At At At At At At At At At At At At At	3.5 per cen 4 per cen 2 per cen	t of investment it of investment it of investment		
Persentation	3.5 per cen 4 per cen 2 per cen	t of investment t of investment		•* <b>*****</b> *****
Pepervision	3.5 per cen 4 per cen 2 per cen 1 per cen	t of investment it of investment it of investment		3,000
Pepervision	3.5 per cen 4 per cen 2 per cen 1 per cen Tor	t of investment t of investment t of investment t of investment		3,000

#### TABLE 7. 80,000 TONS/YEAR ETHYLENE PRODUCTION

Unit 2. Ethane and propane steam-cracking

	Annual cost (104 \$US/year
SELLING PRICE	
Net cash flow at 20 per cent * of total investment	2,600
Depreciation provides	1,630
Net income after taxes a second second second second second second second second second second second second se	970
Net income before taxes at 50 per cent	1,940
Manufacturing cost	7,871
Total sales	9,811
By-product sales	
Propylene-propane (30,000 tons/year at \$30/ton)	
Butylene-butadiene (4,500 tons/year at \$30/ton)	
Gasoline (4,500 tons/year at \$22/ton)	
Fuet oil (1,500 tons/year at \$15/ton)	
TOTAL BY-PRODUCTS	1,156
Ethylene sales	8.655
Ethylene selling price (\$/ton)	108
(or ¢/lb)	4.9

\* Return required for a five-year payoul.

## IV.1.2.D. Effect of feed and by-product values

The marked effect of naphtha, ethane and propane feed value on ethylene selling price is illustrated in figure III for the two units, using the base case values for fuel and by-products.

It is seen that unit 1, based on naphtha steam-cracking produces the largest amount of by-products. It results that the evaluation of these by-products would have in this case a large effect on ethylene manufacturing cost and hence also on the selling price. These data are presented in table 8.

## Hypothesis

1

Case 1. 50 per cent of propylene produced are valorized as petrochemical feed-stock at \$US 55/ton (\$\epsilon 1b 2.5).

Case 2. The whole propylene is valorized at SUS 50/tonand the C<sub>4</sub> cut is sold at SUS 60/ton for butadiene

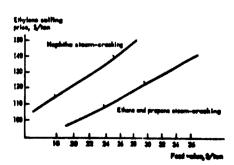


Figure III. Effect of food value on onlyions price

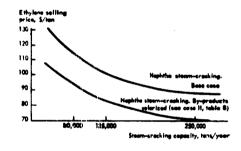


Figure IV. Economics of plant size and effect of by-products value

extraction, assuming an equivalent unseparated butadiene value of \$120/ton.

# IV.1.2.E. Economics of plant size

Ethylene plants with a capacity of about 200,000 to 250,000 tons/year are now planned in Europe. The economics that such large plants have to offer are presented in figure IV above. The cost structure is based on the unit 1-naphtha steam-cracking.

This figure indicates that a larger unit is highly attractive because of lower selling price due to the economics of size. However, the graph shows that plants of a capacity of 125,000 to 150,000 tons/year are already approaching the flat part of the curve and that there is only a difference of about 8 per cent between the selling prices of ethylene obtained, respectively, on a 150,000 tons/year and a 250,000 tons/year plant. Also it is necessary for huge

	Base	Case	Can	<b>r</b> 1	Cas	Case 3			
	Annual quantity (tons/year)	Selling price (\$/ton)	Annuai quantity (tonsiyear)	quantity price quantity					
Егрес	T OF BY-PROI	DUCTS VAL	UE AND INCRE	ASE OF DE	MAND				
Propylene-propane	t of by-proi 51,000	30	UE AND INCRE ( 26,000 25,000	30	MAND 51,000	50			
Propylene-propane			∫ <b>26,00</b> 0		51,000				
Errac Propylene-propane Butylene-butadiene Gasoline	51,000	30	26,000 25,000	30 55	1	50 60 22			

# TABLE 8. 90,000 TONS/YEAR ETHYLENE PRODUCTION Unit 1. Naphtha steam-cracking

plants to be run at or near full capacity if they want to compete favourably with the plant whose capacities are lying on the flat part of the cost/capacity curve.

# IV.2. ACETYLENE PRODUCTION

# IV.2.1. Limited outlets for acetylene

The growth rate for acetylene is slow because of competition from lower priced ethylene and propylene. For example:

The trend to base acetaldehyde production on direct oxidation of ethylene instead of hydrolysis of acetylene.

Partial loss of acrylonitrile markets to the propylene ammonia route.

Potential loss of vinyl acetate markets to ethylene. Improvements to butadiene by butane or butene dehydrogenation.

The major market for acetylene is PVC, and acetylene will continue to share this market with ethylene, the choice depending on hydrocarbon availability, price, and the chlorine balance problem.

TABLE 9. 33,000 TONS/YEAR ACETYLENE PRODUCTION Natural gas-based partial oxidation process

	Europe	Developin country
OPERATING COST ELEMENTS		
investment (grass roots plant) (MM \$ US)		
Process units		
Oxygen unit	4.2 6.4	
Total	10.6	
Off-sites (including power generation)	6.1	
Start-up expenses	0.6	
TOTAL INVERTMENT	17.3	22.5
aw material balance		
Natural gas (Nm <sup>3</sup> /hr)		
felloles		
Beetricity (included in natural gas consumption) Steam produced (tons/br)		
Treated water (m <sup>3</sup> /hr) 90		
	Barepe	anniny
Nemicals and catalysts	650,000 15	700,000
apallier		acetyles

# IV.2.2. Acetylene sources

Due to the rising costs of coal and electric power, the carbide-based acetylene process is now less attractive in Europe, and expansion of acetylene capacity will be based on natural gas and naphtha.

However, in certain locations and under specific conditions, the carbide-based process may be more attractive where off-take electricity is available at favourable rates.

## IV.2.3. Acetylene processes

Only three companies have substantial experience of licensing their processes to third parties: BASF, SBA-Kellogg and Montecatini. All these processes are similar in that they depend on burning part of the hydrocarbon feed with oxygen in order to raise the temperature of the remainder of the feed to a level at which acetylene is formed. Acetylene formation is followed immediately by a rapid quench to prevent the acetylene from decomposing again.

## TABLE 10. 33,000 TONS/YEAR ACETYLENE PRODUCTION Natural gas-based partial oxidation process

(Erected in Europe)

			Unit	Unit cost (\$US)	Annual <b>enantit</b> y	Annual cool 10° \$/year
	MANUFACTURING	COST	AND SELLING	PRICE		
Variable costs						
Raw material balance						
Natural gas Residual gas (credit)		•••	10 <sup>e</sup> m <sup>e</sup> 10 <sup>e</sup> koal	13 1.5	246,000 1,010,000	33 <b>,20</b> 0 ( 1 <b>,500</b>
Utilities					• •	、 - <b>,</b>
Treated water	• • • • • • • • •		m <sup>a</sup> To <b>ns</b>	0. <b>2</b> 1.6	720,000 66,300	360 ( 106
		•••		1.0	00,500	
=	••••	•••				650
Labour and supervision						
Salaries and wages . Supervision	•••••	••	Men/year At 25 per cent of salaries	5,000	60	300
			and wages			75
Royalties	· • • • • • • • •	•••		6	33,000	196
Тот	AL VARIABLE CHAR	GES				3.177
Fixed costs						
Depreciation			17.6	-		
Interest		At	12.5 per cent		investment	
Maintenance		At			investment	
<b>General Plant Overhead</b>		At			investment	
Taxes and Insurance .	• • • • • • • •	At			investment	
Tor	AL FIXED COSTS					4,000
MAX	UFACTURING COST					7.177
Selling price						
Net cash flow at 20 per	cent h of total in					
Depreciation provides .	cent " Of total in	vuolis		• • • •	•••••	3,460
Net income after taxes	· · · · · · · · · ·			••••	•••••	2,100
Not income before taxes	at 50 per cent	• •	••••••	• • • •	• • • • • •	1,300
Manufacturing cost			• • • • • • • •	••••	• • • • • • •	<b>2,000</b> 7,177
Acetylene sales	••••					9,777
Acetylene selling price (\$	(1)\$/ton)	-				
	κ (//b)	•••	••••	••••	• • • • • • •	13.5

· Return required for a five-year payout.

# TABLE 11. 33,000 TONS/YEAR ACETYLENE PRODUCTION Natural gas-based partial oxidation process

(Erected in a developing country)

and the second the available the	<b></b>	Unit	Unit cost (BUS)	Annual Quantity	Annual con 10ª \$/year
MANUFAC	TURING COS	T AND SELLIN	ig price		
Variable costs					
Raw material balance					
Natural gas		10° m²	6.5	246.000	1.00
Residual gas (credit)		10 <sup>e</sup> kcal	0.8	1.010.000	1,60 ( 80
Utilities				110101000	( 00
Treated water		m <sup>s</sup>			
Steam (credit)	•••••	Tons	0.2 1.4	720,000 66,300	36
Chambrida and a dit a			1.4	00,300	(- 9)
•	••••				700
Labour and supervision					
Salaries and wages	• • • • • •	Men/year	6,000	60	360
Supervision	• • • • •	At			
		50 per cent of salaries			
		and wame			90
Royalties		ana wa <b>je</b> e	-		
	• • • • •		6	33,000	19
TOTAL VARIA	LE CHARGES				2,407
Fixed costs					
Loan repayment, depreciation and total investment	interest for	equity capits	ul at 18.5 p	er cent * of	
Maintenance		At 4 per or	ent of total	investment	
General plant overhead	• • • • •	At 2 per or	ent of total	investment	
Taxes and insurance	••••	At I per c	ent of total	investment	
TOTAL FIXED	0081				5,750
MANUFACTURI	NG CORT				
					8,157
elling price					
Not cash flow at 20 per cent b equ	aity capital	• • • • • •			1,490
Depreciation on equity capital pro	vides			• • • • • • • • • • • •	
Depreciation on equity capital pro Net income after taxes	vides	• • • • • •	• • • • •	· · · · · ·	930
Net income after taxes	vides	· · · · · · ·	• • • • • •	· · · · · · · · · · · · · · · · · · ·	930 550
Depreciation on equity capital pro Net income after taxes	vides	· · · · · · ·	• • • • • •	· · · · · ·	930 550 1,100
Net income after taxes	vides	· · · · · · ·	• • • • • •	· · · · · · · · · · · · · · · · · · ·	930 550 1,100 8,137
Depreciation on equity capital pro Net income after taxes Net income before taxes at 50 per Manufacturing cost	vides	· · · · · · ·	• • • • • •		930 550 1,100

\* Calculated as follows: short-term loan repaid at 25 per cent of 1/3 of total investment; long-term loan repaid at 15 per cent of 1/3 of total investment; depectation and financial charges on equity capital at 16 per cent of 1/3 of total investment. TOTAL: 18.5 per cent of total investment.

\* Return required for a five-year payout.

Now all three processes can handle naphtha, and ICI, which is considering naphtha for its new 60,000 tons/ year acetylene plant at Runcorn in the UK, chose the BASF process.

IV.2.4. Economics of acetylene production

Taking into account:

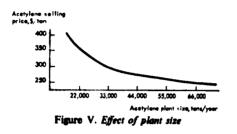
1. The higher investment cost of a naphtha-based plant, because of:

High dilution of acetylene in cracked gases;

Additional investment required by the ethylene co-pro-duct recovery and purification plant;

2. The difficulty for a producer to balance acetylene and ethylene demands which will not necessarily occur at the same location;

the manufacturing cost and the selling price of acetylene in a 100 tons/day plant <sup>6</sup> based on natural gas feedstock have been studied for Europe and developing countries, where natural gas is available at a low price. The elements of the operating cost are given in table 9; the manufacturing cost and the derived acetylene selling price for the two cases are presented in tables 10 and 11.



<sup>4</sup> Corresponding to a 75,000 tons/year PVC production.

ġ,

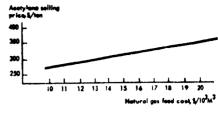


Figure VI. Effect of feed-stock value

The effect of plant size and natural gas feed cost on the economics of acetylene are shown, respectively, in figures V and VI, for units to be erected in Europe.

The acetylene selling price ranges from  $\notin/1b$  11.5 to  $\notin/1b$  13.5 compared with  $\notin/1b$  4.5-5.2 for ethylene selling price.

The selling price of acetylene could be slightly improved if residual gases would be used as a source of synthesis gas for an ammonia or methanol plant located next to the acetylene unit.

# TABLE 12. 44,000 TONS/YEAR BUTADIENE PRODUCTION — HOUDRY BUTANE DEHYDROGENATION AND PHILLIPS FURPURAL EXTRACTIVE DISTELLATION

	<b>)0</b>	\$US
	Europe	United State
OPERATENG COST ELEMENTS		
Presetment (grass roots plant)		
Process units . Off-sites, including utilities and auxiliaries required for a self-sufficient installation .	15.40	16.20
Initial catalyst and chemical charges	0.64 1.00	0.60 1.00
TOTAL	17.04	17.80
Material balances		
Raw material: n-butane		
Utilities requirements		
Fuel (10° Kcel/year)         312,000           Electricity (kWb/year)         13,000,000           Treated water (10° m²/year)         280		
	\$U	Norman
-	Arrepo	United States
Catalyses and chemicale regultremente	650,000	630,000
Mentality	18	
	10	

# **IV.3. BUTADLENE PRODUCTION**

# IV.3.1. BUTADIENE SOURCES

The butadiene raw material situation in Europe is also somewhat different from that in the United States. Production of  $C_4$  in the United States in 1962 totalled 36.10<sup>6</sup> tons, primarily as butane from natural gas and butane/butylenes refinery streams.

The biggest petrochemical market for  $C_4$  streams is butadiene, obtained by butane dehydrogenation, butylene dehydrogenation or as a co-product in ethylene plants.

In Europe, butadiene production has been based on refinery butylenes and on butadiene extraction from naphtha steam-cracking plants which are expanding rapidly. The butadiene can be extracted relatively simply from the other  $C_4$ 's produced in the same way that the butadiene product is extracted from the reactor effluent of a dehydrogenation plant. Typical extraction solvents are cuprous ammonium acetate, acetonitrile and furfural.

# **IV.3.2. DISTRIBUTION OF PROCESSES**

In the United States the dehydrogenation of butylenes is still the dominant process, but the one-step Houdry process is making considerable strides. The choice between these processes is largely influenced by the availability of feed associated with large refinery installations.

TABLE 13. 44,000 TONS/YEAR BUTADIENE PRODUCTION — HOUDRY BUTANE DEHYDROGENATION AND Phillips fulfural extractive distillation (rescted in Europe)

	Unit	Unit cool (SUS)	Annual quantity	Annal cost (10° \$/your)
	NG COST AND	BUTADIENS SELL	ING PRICE	
Variable costs				
Raw material				
n-butane	Tons	32	80,000	2,560
Utilities				·
Pool.	10 <sup>s</sup> Koal	1.5	312,000	468
Electricity	10° kWh	10	13,600	136
Treated water	<b>38</b> <sup>4</sup>	0.2	290,000	58
				662
Catalyst and chemicals.				630
Labour and supervision				
Salaries and wages (mon/year).		5,800	72	300
Supervision at 25 per cent of salaries and wages				
				<u> </u>
Rovekies.	-			450
	Tens	13.8	44,000	610
TOTAL VARIABLE COSTS				4,952
Read asses				
Depreciation		At 12.5 per es	nt of immediates	
Interest			at of investment	
Maintenance	• • • • •		at of investment	
General plant overhead	• • • • •		at of investment	
	• • • • •	At 1 per cel	nt of investment	
TOTAL PECED CONS				3,939
MANUACTURING CUT				
folling price				-
Net each flow at 20 per cent " of to	ini Jamainani			
Dependation provides		•••••	• • • • • • • •	3,400
Nat income after taxes		••••••••	•••••••	1.389
Net income before tense at 50 per e			••••••	2.50
Dutvillane aufes	• • • • • •			11.412
				200
	• • • • • •			

· Return required for a five-year payons.

	Unit	Unite anat (\$US)	Annual quantity	Annual or ( 30° \$/;=0	
MANUFACTURIN	G CORT AND		ING PRICE		
Variable costs					
Raw material					
a-butane	Tons	24	88,000	1,3	981
Utilities					
Fwel	10° Koni	1.0	312,000	312	
Electricity	ið kWh	•	13,000	100	
Treated water.	181 <sup>8</sup>	0.2	290,600	<b>98</b>	
					479
Catalyst and chemisals				•	630
Labour and supervision					
Salaries and wages (men/year).		7,688	72	550	
Supervision at 25 per cent of salaries and wages				137	
				•	881
Royalties	Tens	13.8	44,000		614
TOTAL VANABLE COSTS				4.1	101
lined sects					
Depreciation		t 12.5 per cent	of investment		
Interest	🔺	it 3.5 per cont	of investment		
Comment along to the state			t of investment		
Tanes and insurance	· · · · / A	-	t of investment		
TOTAL PINES COPPE		-			
MANUFACTURING OBST				M	186
felling price					
Not each flow at 20 per cent * of ter	tal investment			ы	10
Depresiation providue				<u>i</u>	
Not income after taxes				1.1	
Not income before taxes at 52.5 per	• • • • • • • • • • • • • • • • • • •		· · · · · · ·	<b>ਮ</b>	
Manufacturing cost	• • • • • •			M	_
				11,2	
				-	

TABLE 14. 44,000 TONS/YEAR BUTADERIE PRODUCTION --- HOUDRY SETANE BENYBROGENATION AND PHELLIPS PURPURAL EXTRACTIVE DISTILLATION (BRECTED ON UNITED STATES GULF COAST)

· Return required for a five-year payout.

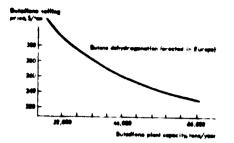
Where there is a considerable availability of cat. butylenes, it is likely that the butylene dehydrogenation process would be chosen (Esco Petroleum at Fawley, England). In Germany, on the other hand, the Hills plant selected dehydrogenation of n-butane, since it was felt that there were no adequate supplies of cat. butylenes available to form the basis of a fully economic plant.

1.1

In Burope, now, where othylene productions from neghths steam-cracking are sufficiently large, it may be well worth while to entrust butadisme from the  $C_6$  out, since it becomes a valuable co-product with othylene.

# IV.3.3. ECONOMICS OF BUTADIME PRODUCTION

## A. Dutane dehydrogenation by Nowby process





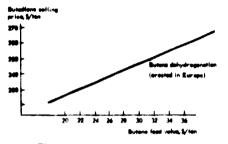


Figure VIII. Effect of butane value

# TABLE 25. 16,000 TONS/YEAR BUTADIENE EXTRACTION (Plant erocted in Europe)

	Accionatrile process Shell	( 4.4 process Esso	Furfural extraction Phillips
Operating	COUT BLEM	ENTS	
Investment (SUS million)			
On-site Off-site	1.5 0.6	2.6 0.6	2.0 0.6
TOTAL INVERTMENT	2.1	3.2	2.6
Utilities			
Steam (tons/hr). Fluetrialty (kWh) Cooling water (10 <sup>s</sup> m <sup>2</sup> /hr)	32 110 8,0 <b>0</b> 0	8.4 1,210 1,7 <b>2</b> 0	20.5 160 2,870
Chemicals requirements/year	\$25,000	\$25,000	\$60,000
Repairies	\$8.25/ton*	\$8.25/ton*	5
Labour (mon/shift)	4	4	4

· Running royalties paid during eight years.

\* Paid-up royalties included in investment cost.

Also, United States butadiene producers whose plants are already amortized, can export to Europe at landed prices which are below their own domestic prices.

The elements of the operating cost for a 44,000 tons/ year butadione plant which could be envisaged to be built respectively in Europe and in the United States are presented in table 12.

The manufacturing costs for the two cases are given in tables 13 and 14 and the corresponding butadiene solling prices are derived.

The effect of plant size and butane field cost on the economics of butadione production are shown respectively in figures VII and VIII for units to be erected in Europe.

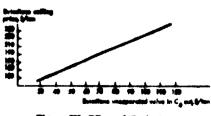
# **D.** Dutadiene extraction from C4 cut produced in ethylene production by the cracking of nightsha

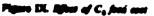
Since only a process of extraction is involved, the minimum scale at which it is economic to extract coproduct butadiene is smaller than that for butadiene synthesized from n-butanes or n-butane. This minimum economic scale depends on several factors, namely: The quantity of butadiene available in the C<sub>4</sub> stream; The concentration of butadienes in the total C<sub>4</sub> stream; The nature of the other C<sub>4</sub> constituents.

The conditions of crecking, which give both a high yield of other and an exit gas competition feveurable to the separation of pure obviews at minimum cost, are by and large also these which give a good concentration of batadiene in  $C_{\rm c}$  out. Also Burepann obviews producers who have the tendenty to go to more arvare conding with higher yields of obviews are in a good producers to rapply batadiene at a lower point. The elements of the operating cost are presented in table 15 for a 16,000<sup>7</sup> tons/year butadiene extraction plant using, respectively, the CAA process from Esso Research and Engineering Co., the Acetonitrile process from Shell and the Furfural extractive distillation from Phillips. The manufacturing cost and the butadiene selling prices for the three cases are given in table 16. The effects of C<sub>4</sub> feed cost on the selling price of butadiene are shown in figure IX for the Acetonitrile process.

As can be seen, the cost of butadiene produced in a 44,000 tons/year European unit by butane dehydrogenation ranges from approximately SUS 260/ton to SUS 290/ton, according to butane feed cost varying from SUS 32/ton to SUS 50/ton. The selling price of extraction butadiene by Acetomitrile process, in the same range of  $C_4$  cost is much less (are figure VII) for a smaller production (16,000 tons/year), and if it is accumed that the othylene production bears all the capital cost of the nephtha cracker and that the butadiene is charged to the extraction plant at fuel value, a butadiene cost of about SUS 120/ton can be achieved.







## TABLE 16. 16,000 TONS/YEAR BUTADREME EXTRACTION

(Plant erected in Europe)

		Luit cost	4000	onis i le	ć	Partural		
	Contraction of the second second second second second second second second second second second second second s	·\$E(\$)	Annual Quantity	Annual cost 10° \$	Annual Annual cost quantity 10* \$		Annual quantiy	Annual con
	MANUFACTUR	NG COST ANE	SHELLING	PRICE				
eriable costs								
Raw material *	Tons	32	16,500	527	16,599	527	16,589	527
Steem	Tone	1.6	256,000	410	67,000	107	164,500	263
Electricity	10° kW	10	880	9	9,780	97	1,200	13
Cooling water	10° m²	6	8,800	44	1,720	10	2,870	17
Chemicals requirements								60
Labour and supervision								
Salaries and wages		5,000	16		14		16	80
Supervision				-				-
	salaries and wages			20				20
Running royalties				132		132		
TOTAL VARIABLE CHARGES				1,251		998		900
lixed charges								
Depreciation	At 12.5 per cont of inve	iment						
Interest								
	At 4 per cont of inves							
	At 2 per cent of inve							
Taxes and insurance	At 1 per cent of inver							
TOTAL PINED COSTS				400		735		
MANUFACTURING COFT				1,791		1,733		1, 500
letting price				and a spine of a state of the spine of the s		and an approximation of the second		
Not each flow at 20 per cent of								
total investment				430		660		520
Depreciation provides				200		480		320
Not income after taxes				100		240		200
Not income before taxes at 50 per				-				
Manufasturing cost.				339 1.731		1.733		1.500
						1,733		
Butadione sales				2,051		2,213		1,900
Detadlane softing price			SUB .	130		140		125

. Butadiens in C, out.

8

11

#### IV.4. AROMATIC HYDROCARBONS PRODUCTION

### IV.4.1. INTRODUCTION

Instead of oval, petroleum has emerged as the dominant source for at anatic chemicals. It has now encoded all other raw materials as a source for beamene and it has been ahead of other sources for toluene and zylanes since 1950.

These changes in aromatic raw material sources were all brought about through accessity, and will have forreaching efforts on the industry:

Petroleum refinere new have an important entry into petrochemicale, through control of the row materials supply and will be able to utilize and upgrade various by-product streams;

- The abundance and low eact, of these materials will encourage even more the development of new derivatives and new processing techniques.
  - IV.A.2. Алематис вольсав рассмятном ог так БЛУ РЕОССИЯН

## The processes which serve for:

Pasevery of BTX from potentisum streams; Hydrodenikylation of mathet accordin; Separation of individual aromatics from BTX, notably in the C<sub>0</sub> fraction;

will be studied hereafter.

#### IV.4.2.A. Recovery of BTX fraction

BTX is recovered from the gasoline fractions produced in the course of catalytic reforming and ethylene production by naphtha steam-cracking. Conventional separation of BTX from non-aromatic components in the same boiling point range involves the following routes:

Extraction by solvents, notably: diethylene or triethylene glycols, sulfolase, dimethyl sulfoxide, N methyl pyrrolidone and morpholene;

Extractive distillation;

Azeotropic distillation;

#### Adsorption.

Of these four approaches, extraction has proven the most versatile method, capable of operating effectively with a wide range of feed-stock, and very high product purity can be achieved by this route.

# IV.4.2.B. Hydrodealkylation

The potential availability of toluene from BTX fractions is nearly 5 to 7 times that of benzene. This situation is the reverse of the relative domand for these two commodities.

The answer to the benavne supply problem has come with the large-scale construction since 1960 of hydrodealkylation plants which can convert surplus tolusne to benavene equivalent in quality to extraction benaves.

So, encose toluens most frequently used in gasoline pool of the refinery at a lower profit realization than either the benzene or xylenes sold for petrochemical purposes can be purchased at a reasonable price and converted into high purity benzene.

# IV.4.2.C. Separation of C<sub>2</sub> aromatics

While distillate separation of bensome and tobases from other aromatics presents no problem, serious difficulty is encountered in isolating the components of the  $C_0$  aromatics fraction, as can be seen from the following boiling point spread:

ethylbenzer	16	•	·									136.1°C
p-xylene	•	•		·								138.5°C
m-xylene	•											139.1°C
o-xylene .				•	-				•			144.4°C

All four of these components are today recovered as chemical feed-stocks. Ethylbenzene, purified by superfractionation, is dehydrogenated to styrene. For the three isomeric xylenes, the principal market is in oxidation processes to the corresponding dicarboxylic acids.

The least difficulty in purification is encountered in the case of o-xylene which is readily separated by distillation.

The recovery of ethylbenzene is effected by superfractionation and is of economic interest only in conjunction with xylenes production. However, the bulk production continues to be based on ethylene and benzene.

Para-xylene's importance hinges almost exclusively on its role as intermediate product in the manufacture of terephthalic acid. It is impossible to isolate p-xylene by distillation, and tractional crystallization must be used.

Meta-xylene is the racet important member of the C<sub>0</sub> aromatics; it is used either as petrochemical feed-stock for isophthalic acid manufacture or into gasoline blends and into solvents. An alternative solution is to isomerize m-xylene to the para and ortho compounds.

### IV.4.3. ECONOMICS OF ABOMATIC PRODUCTION

It is difficult to generalize the economics of the different processes utilized in aromatics manufacture as:

Catalytic reforming; Extraction; Hydrodealkylation; Superfractionation:

Practional crystallination:

because of the diverse characters, values and potentials of the technically feasible charge stocks. Nevertheless, the economics of a typical aromatics plant designed to produce: beanene, tohuene, o-xylene and p-xylene and based on the different processes described above, will be studied in chapter 'II, where an example of an integrated petrochemical complex is given.

# 2. NATURAL GAS AS A RAW MATERIAL FOR PETROCHEMICALS

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### A. BASIC INDUSTRY REQUIREMENTS

A nation's potential for petrochemical production must be assessed from three main points of view:

- 1. Availability of natural gas or petroleum feedstocks,
- 2. Degree of industrial sophistication; and
- 3. Access to end-use markets.

The first of these requirements is axiomatic. By its very definition, the petrochemical industry uses petroleum or natural gas as one of its major raw materials. But these two types of feedstock are, economically speaking, not strictly interchangeable.

Even technical interchangeability is limited. Natural gas provides a basis only for the manufacture of the lower aliphatic petrochemicals, and for the production of carbon black and the derivatives of synthesis gas, notably ammonia, methanol and their end products.

All of these chemicals can also be synthesized from oil or, for that matter, from coal. However, from an economic point of view it is found that natural gas is the raw material *par excellence* wherever it is available at low cost. This is a somewhat qualitative statement which will be substantiated in some more detail later. In general terms it means that natural gas is favoured over alternative chemical feedstocks at consumer points which have pipeline access to natural gas fields. More recently, the economic appeal of natural gas has even been extended to chemical consumers who can receive this fuel in liquefied form via marine shipment, and this development may be expected to have a significant impact on the future geographical distribution of petrochemical plants.

The second point mentioned above suggests that a mation's potential for petrochemical production is affected by its degree of industrial sophistication. Aside from their hydrocarbon feedstock, petrochemical plants draw on a vast array of other raw materials, process chemicals and operating supplies. They require ready access to replacement equipment and to the equipment manufacturer's technical advice. And, in large measure, the stimulus for petrochemical growth seems to be related to the availability of skilled technical personnel and to their ability to communicate readily with their colleagues in related industries.

To a large extent, it is also only in advanced industrial societies that we find the markets which alone can support a broad petrochemical industry — and this brings us

to the third point mentioned above which bears a little further examination.

At an early stage of industrialization, a nation may find it advantageous to produce only some of the basic end-use commodities from natural gas. Above all, this means sulfur and ammonia to meet the country's own growing agricultural demands and possibly for export to some of the neighbouring States. Maybe the next step will be the production of some detergents and paint raw materials from hydrocarbon feedstocks. But it will be quite a jump from here to the production of polymers which find their markets, not directly in the hands of the end consumer but in converter industries moulding or extrusion plants in the case of plastics, largescale spinners, weavers, dyers and other converters in the case of resins for synthetic fibres and their raw materials.

Where are these markets to be found? Until they become adequately available within the developing nation, the petrochemical producer will have to look for special situations which warrant production of some intermediates, such as butadiene or methanol, for export. However, even when special situations develop which justify petrochemical production primarily for export, they will be exactly that — special situations which are not an adequate basis for a broad petrochemical industry.

On the contrary, the biggest attractive force for both refining and petrochemical centres are the large industrial population areas and the migration continues toward them as low-cost means for transportation become available for crude oil and natural gas.

We see this trend already established in refining. Prior to the Second World War, the world's great refining centres were located in the crude oil production regions — Indonesia, Venezuela, Iran. Texas and Oklahoma, etc. In the post-war era, extensive refining capacity came to be built near the consuming centres. Both in western Europe and in Japan, the initial wave of construction was in the areas of deep-water harbours — Hamburg, Rotterdam, Southampton, Le Havre, the Yokohama district, etc. More recently, with the construction of large petroleum and gas pipelines into the heart of western Europe, a new wave of inland refinery construction has taken place, near Cologne, Strasbourg, Karlsruhe, and Ingolstadt. This will certainly be followed by major petrochemical development in these areas.

Such trends are in line with the observation that an economically sound, diversified petrochemical industry can be supported only by mass markets. This is so because the unit cost of most manufacturing operations in this field is strongly influenced by plant size. Thus, the spread of petrochemical centres receives strong impetus from the evolution of large consumer markets with minimum trade barriers.

The United States petrochemical industry has long enjoyed the favourable labour and investment costs which are associated with the large production units feasible within its economy. A market of similar magnitude is quickly taking shape within the European Economic Community. Future South-East Asian and Latin American trading communities are now only in the talking stage but experience has shown that such a development would certainly provide a major stimulus to industrial growth within these regions.

So far, this discussion has dealt with the requirements for a broad, diversified petrochemical industry. Although such an industry must await the evolution of a strong industrial base within any given marketing area, there are significant opportunities, even for the developing nations, in upgrading a part of their local hydrocarbon resources by chemical conversion.

This opportunity is principally in those commodities which are relatively close to the end market --- notably ammonia, sulphur, possible ethylene glycol and carbon black, and the raw materials for some of the lowercost polymers - ethylene, vinyl chloride, styrene, butadiene, methanol and formaldehyde. All of these products are derived, at least in part, from natural gas - and in most instances, a low-cost source of natural gas constitutes the optimum raw material. Just for the sake of completeness, it should be mentioned that some surfactants also fit into early stages of a nation's developing industrial economy, but these products draw, in the main, on a raw materials base available only from heavier petroleum fractions, especially now that the call is for biodegradable detergents. Such surfactants are, therefore, outside the scope of my discussion.

But that still leaves natural gas with a very broad and significant position as raw material for the petrochemical industries of both developing and advanced industrial economies. It may be well now to examine why this is so, and to take a look at the prospects of the main derivatives of natural gas and at the competitive economics of other raw materials.

It is, of course, the primary purpose of this meeting to assess the petrochemical industries as they may be applicable to developing countries. Despite this, frequent reference will have to be made to the situation in the United States and in Western Europe, This is necessary, not only because the petrochemical picture in these two regions is already fairly well charted, but also because their experiences can be used as prototype for the petrochemical future of other areas. Thus, the United States is the prototype of a highly industrialized nation which has been building up its petrochemical industries for over thirty years now. Western Europe, on the other hand, is the example of an industrially advanced area in which petroleum and natural gas as chemical feedstocks have come to the fore principally during the last four or five years. Here, hydrocarbons are replacing previously entrenched raw materials, namely coal and coke, as feedstock for many previously established chemical operations.

For a more detailed examination of natural gas as chemical feedstock, it is first necessary to define the sources of natural gas and take a look at the chemical components which make it so valuable as raw material for the petrochemical industries.

# B. NATURAL GAS - SOURCES AND COMPOSITION

The term "natural gas" is applied to all varieties of gas produced from underground rocks, in which the paraffin series of hydrocarbons predominates. The gas is produced in three types of reservoir:

(1) Dry-gas reservoirs in which the gas is accompanied by only relatively small amounts of liquid hydrocarbon when it is reduced to atmospheric pressure and temperature;

(2) Condensate reservoirs in which the gas is accompanied by larger amounts of liquid hydrocarbon; and

(3) Oil reservoirs in which the gas may be either "gas-cap" gas from the crest of the reservoir or solution gas liberated from the oil as pressure is reduced in the production process.

At normal pressure and temperature, the gaseous hydrocarbon constituents of natural gas are principally methane and ethane, together with varying small amounts of heavier hydrocarbons. In almost all cases, olefins are absent from the gas as it emerges from the ground. Impurities in the gas include principally nitrogen, carbon dioxide, and hydrogen sulfide. Helium is sometimes present in recoverable concentration.

Natural gas composition varies widely from field to field. Even the gas obtained from a given well does not always remain constant in composition over the life of the well. Just by way of illustration, table 1 shows two American natural gases. Methane content in these two particular gases ranges from 68 to 84 per cent and hydrogen sulfide content is zero and 6.8 per cent, respectively.

#### TABLE 1. NATURAL GASES SEPARATED PROM CRUDE OILS OR CONDENSATES

iald	Oklahoma	McKamin Arkansas 260
Imperature	67	65
empeatition, mole per cent		
N <sub>P</sub>	-	11.1
<b>CO</b> <sub>1</sub>		
H <sub>4</sub> 8	-	6.8
СН	83.9	68.3
С.Н	9.7	7.2
С.Н	3.9	3.3
<b>ČrČ</b> ,	2.5	2.7

The last few years have seen very significant new discoveries of natural gas fields. Some of these discoveries are accessible to the great industrial centres of Western Europe and are responsible for a basic shift in the European raw materials base. Among these discoveries, mention should be made of the fields at Lacq in France, Groningen in the Netherlands, Italy's lower Po valley, and the Saharan fields in Northern Africa. At the same time, distribution of natural gas is being facilitated, thanks to the marine transportation of liquefied natural gas and the construction of new pipeline networks.

Table 2 shows the enormous growth in proved natural gas reservoirs around the world which has taken place between December 1959 and mid-1963. The first of these estimates was made by the U.S. Bureau of Mines, the second, by the U.S. Geological Survey. It should be pointed out, however, that these are only educated guesses made on the basis that 6,000 cu.ft. of gas are expected per barrel of oil. Actual field-by-field estimates of proved gas reserves are not available on a world-wide basis. The most recent estimate suggests world-wide reserves of 1.8 quadrillion cubic feet natural gas. Two-thirds of these reserves are located in the Middle East.

TABLE 2. ESTIMATED PROVED WORLD GAS RESERVES

	December 1959 (U.S.B.M.)	<b>MM-1963</b> (U.S.G.S.)
Total reserves, cu. ft	660 trillion	1.8 quadrillion
Location		
Middle East	30 %	65 %
North America.	42 %	16 %
Countries with centrally plan-		
ned economies	12 %	10 %
Venezuela	6%	6%
Other	10 %	3%

Of course, the markets are not always where the reserves occur and there is a great disparity in the world distribution of gas fields on the one hand and of marketed natural gas production on the other. Figure 1 shows the production of natural gas during 1958 and 1962, but it includes only marketed output. Gases used for repressuring and gases flared, vented, or otherwise wasted are excluded from the data. It is seen that world-wide output has risen from 13.8 trillion cu.ft. in 1958 to 19.7 trillion cu.ft. in 1962, an increase of nearly 43 per cent. But almost the entire marketed production of natural gas during those years has occurred in the highly industrialized regions of North America and Europe. Together. these two continents accounted for 96.3 per cent of total production during both 1958 and 1962. The bulk of "European" production is of Russian origin, which accounts for over 60 per cent of this sub-total.

This relative distribution is bound to be strongly affected by the discovery of major gas fields in Europe and by the prospect of improved gas transportation.

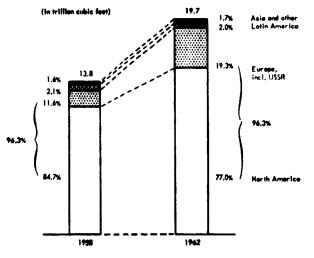


Figure I. Marketed production of natural gas

Thanks to marine shipment of liquefied natural gas and to new pipeline construction, European markets are becoming increasingly accessible to gas produced in the Middle East and in North Africa.

## C. TRENDS IN GAS UTILIZATION

The preoccupation of this meeting with petrochemical conversions must not obscure the fact that the price of natural gas is set by its value as fuel. This, of course, is the primary demand for natural gas. Thus, in the United States, natural gas distribution to different sectors of the economy has been estimated as shown in table 3.

Direct energy uses account for 50.7 per cent of gas consumption while the chemical industries consume only six per cent of this total. This includes both process and fuel uses in chemical manufacture. As a source of energy, the limiting value of natural gas must be viewed in comparison with competitive fuels, namely oil and coal. This is, however, not simply a comparison on the basis of BTU value. On that basis alone, a gas priced at 20 cents/million BTU would obviously be

#### TABLE 3. CONSUMPTION PATTERN FOR NATURAL GAS (INCL. REPINERY GAS) (United States, 1962)

Total consumption: 13.8 trillion ou ft.

Residential	24.7 %
Commercial	8.7 % Bargy use = 50.7 %
Electric generation	
Chemicals and allied	6.1 %
Petroleum refining.	4.7 %
Iron and steel	4.5 %
All other industrial	19.2 %
All other	14.8 %

competitive with a typical bituminous coal rated at 13,750 BTU/lb. and costing \$5.50 per ton which also calculates to 20 cents per million BTU.

But the comparison must also take account of the burner equipment's efficiency and its investment and operating costs. To be sure, the efficiency of modern coal burners is comparable to the 80-85 per cent which can be achieved with gas burners, so that the efficiency factor is of principal concern in comparison with older coalburning equipment cost.

Investment and operating costs, on the other hand, are a different story. Table 4, which is based on a recent analysis by Monsanto's John Buss, shows a cost comparison for typical modern steam plants firing coal and natural gas, respectively. At an 80-85 per cent efficiency for both fuels, a natural gas price as high as 42 cents per million BTU is competitive with coal priced at 20 cents per million BTU.

This is the primary reason why first the United States, and more recently, Western Europe and Japan have switched extensively from coal to petroleum and natural gas as their primary energy source. The extent of this switch in Europe becomes clear from figure II. Most striking is the rise in oil consumption during the period 1950-1962, namely from 14 per cent to nearly 35 per cent of total energy consumption. During this period, the growth of natural gas consumption has not yet been so pronounced. This is true because most of the period precedes both the most important gas discoveries made in Europe and the construction of major pipelines from the Middle East.

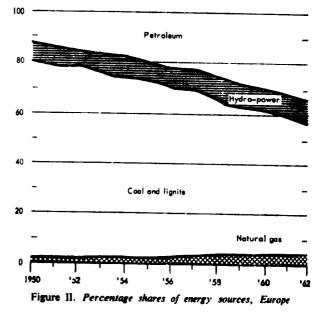
The outlook now is for substantial and fast growth in European consumption of natural gas. A 1960 study by the Energy Advisory Committee of OEEC predicted that Western European markets for natural gas would rise to 100 billion cubic metres by 1975, or about six times the usage in 1962. As in all such forecasts, there is much

TABLE 4. COST OF STEAM GENERATION, COAL VS. GAS

Basis: Coal at 20 ¢/million BTU, 85 per cent efficiency Gas at 30 per cent efficiency

Mark-up for after-tax net return of 10 per cent on incremental capital

	Ceel	Gas
Investment per lb./hr. steam capacity, S Operating costs per million ibs. steam,	10	5
Costs enel. feel, #	24.4 23.6	11.7
	48.0	
Mark-up	16.6	
TOTAL	64.6	(64.6)
Equalization cost		11.7 52.9 42.3



Per cent

disparity in view, however, and in any event consumption is expected to continue its wide variance between countries.

Thus, forecasts during the last few months have variously predicted a 6-10 per cent range for the share of natural gas in covering all Western European energy demands in 1975 — but the Netherlands as a major producer is expected to cover 30 per cent of her own energy requirements during that year by means of natural gas.

As European countries gain access to such large natural gas resources, their chemical industry is also undergoing a transformation, switching such products as ammonia and methanol from a coal base to natural gas. In Italy, the share of hydrocarbons as ammonia raw material rose from 5 per cent in 1952 to 80 per cent in 1962. In France, during the same decade, the rise was from 21 to 45 per cent, largely owing to more extensive exploitation of the Lacq gas fields. World wide, too, the share of natural gas in ammonia production has risen from 30 per cent in 1955 to nearly 40 per cent in 1962. These numbers, it should be noted, do not include the USSR, mainland China or Eastern Europe.

## D. CHEMICAL CONVERSIONS

#### 1. Synthesis gas

We come now to a discussion of the major end-use products for natural gas and, among them, synthesis gas and hydrogen are in a class by themselves. The term "synthesis gas" refers to a mixture of carbon monoxide and hydrogen produced by the reaction of carbonaceous matter with air, oxygen or steam. Three basic kinds of reaction are involved — reforming, combustion and water gas shift, as shown in table 5.

TABLE 5. MAIN REACTIONS IN SYNTHESIS GAS FORMATION Reforming (endothermic)

$CH_4 + H_8O \rightarrow CO + 3H_8$	(1)
Combustion (exothermic)	
$2 CH_4 + O_5 \rightarrow 2 CO + 4H_1 \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots$	(2)
$CH_4 + 2O_3 \rightarrow CO_3 + 2H_8O.$	(3)
Water gas shift	
$CO + H_sO \rightleftharpoons CO_s + H_s$	(4)

In a separate after-processing step, the product's carbon monoxide/hydrogen ratio can be adjusted by the water gas shift reaction which involves the reaction of steam with carbon monoxide as shown in equation 4 in table 5. Thus, synthesis gas is the raw material for ammonia (which requires a hydrogen almost completely free of carbon monoxide) as well as for methanol which calls for a hydrogen/carbon monoxide ratio near 2:1, and for oxo chemicals with a specified hydrogen/carbon monoxide ratio near unity.

Of course, hydrogen has a great many uses other than ammenia and methanol production, and the most important among them are within the refinery — mainly for hydrocracking and hydrotreating operations. An estimate of the relative importance of the various applications for hydrogen in the United States is given in figure III.

#### 2. Ammonia

Ammonia accounts for over 50 per cent of the total demand and will continue to do so — even in the face of the expanding use of hydrocracking. In Western Europe and Japan, where hydrocracking will play a less important role in the total refining picture, ammonia consumes an even greater share of total hydrogen output. Today, wherever natural gas is available at reasonable cost, this is the source par excellence for synthesis gas and hydrogen. In the United States, the share of natural gas as a source of hydrogen for ammonia rose from 11 per cent in 1942 to 81 per cent in 1963. For all countries with free enterprise economies, hydrocarbons (not only natural gas) accounted for 57 per cent of ammonia.

It must be pointed out here that nations and localities which lack access to low-cost natural gas are switching to heavier petroleum fractions as feedstock, a development which has been made feasible especially by the development of sulphur resistant reforming catalysts, such as those of ICl and BASF, and by the availability of noncatalytic partial oxidation processes.

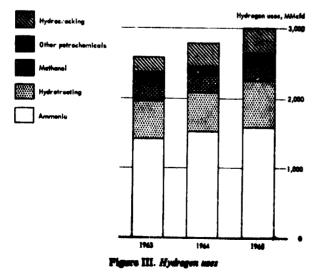
The basic approach in converting hydrocarbons to synthesis gas involves straight steam reforming. This conversion is normally carried out over a nickel-based catalyst. The reaction is highly endothermic and heat requirements are met by passing the process stream through a fired pipestill.

In an alternative approach, which is rapidly gaining in favour, a portion of the process hydrocarbon is burned by air (if nitrogen is not objectionable in the product) or by oxygen. In this way, combustion reactions are allowed to proceed concurrently with steam reforming.

Finally, methane can be catalytically or thermally dissociated to hydrogen by techniques of the type illustrated by U.O.P.'s "Hypro" process.

The synthesis of ammonia by the high-pressure reaction of nitrogen with hydrogen may be considered the most important single reaction employed in the petrochemical industries today. Of course, there are numerous commercial processes and their discussion would lead us too far afield. Suffice it to say that technology is readily available, and that it has reached an extremely high degree of efficiency.

Almost all of the ammonia produced is consumed as fertilizer in one form or another. To be sure, there are other end uses — notably urea-formaldehyde resins and a variety of amines and alkanolarmines — but their consumption of ammonia is only a small percentage of the total.



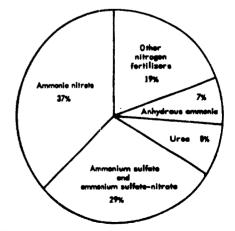


Figure IV. World ninegen firstliner production, 1967 (primary products only)

More important for the ammonia producer is the question in what form he can sell his product as fertilizer. Figure 1V shows the world-wide consumption pattern of nitrogen according to the type of fertilizer in which it is employed. It might be noted in passing that anhydrous ammonia and urea, though they are the smallest portion of the total, are also the fastest-growing end products.

Unfortunately, it must be said that the nutritionally deficient regions will continue to be deficient in fertilizer use throughout this decade and indeed throughout the rest of this century. A study by the Sulphur Institute predicts that total available fertilizer in 1970 will be 125 per cent of requirements in the nutritionally adequate regions but that it will cover only 50 per cent of adequate consumption in nutritionally deficient regions. This is a problem which can be solved only in part by industrialization, and especially by the build-up of capacity for ammonia and other fertilizer ingredients. Of at least equal importance in this situation is the need for farmer education to the benefits of adequate fertilizer use.

A few words should be said here also about urea which is presently in a major growth phase. The product is a derivative of ammonia and carbon dioxide and a number of processes for its manufacture are readily available. The U.S. produced 2 billion pounds of urea in 1962, and output may reach 3 billion pounds in 1966. All but nine per cent of total production is used in fertilizers and animal feed products.

It should be noted in this connection that the buildup of urea capacity is fastest in the developing countries, i.e., nations outside North America. Western Europe and Japan. Their share of world-wide urea capacity is expected to rise from 2 to 3 per cent in 1959 to over 50 per cent in 1966.

### 3. Methanol and formaldehyde

Second major end use for synthesis gas is the production of methanol. U.S. output of this commodity in 1963 was approximately 355 million gallons, an increase of some 5.4. per cent over the previous year. This has also been the average growth rate since 1960 and recent forecasts anticipate an annual growth rate of 4-5 per cent for the next three to five years. Projection at this rate would boost United States production to nearly 450 million gallons in 1968.

Build-up in capacity and demand outside the United States far outstrips this rate of growth. In France, for example, methanol production is expected to rise from 32.5 million gallons in 1963 to 53 million gallons in 1965, and Latin American demand (though not necessarily production) is expected to reach 18 million gallons in 1965 and 84 million gallons in 1970. Indian capacity will grow from nearly nil in 1963 to 13 million gallons in 1965.

A number of outlets combine to create this growing demand for methanol. Of greatest importance is, of course, production of formaldehyde which accounts for nearly one-half of methanol requirements. By comparison, all other outlets are minor, but some of the more important ones are shown in table 6.

# TABLE 6. END-USE DISTRIBUTION FOR METHANOL (United States, estimated 1965)

						_				_		_			
															Per cent
Formaldehyde															47 5
Solvents															7.0
Methacrylales															5.5
Ethylene glycol	•	•	•	·	·				•						5.0
Dimethyl terephthalate	5.	• •	·	·	·	·	·	·	·	·	·	·			4.7
Mothyl halides	•	• •	·	•	•	·	·	•		·	·	·	·	·	
Miscellancous	• •	• •	•	•	•			•							26.7

Included among the "miscellaneous" uses is the synthesis of acetic acid — a process now being installed by Borden Chemical Co. to take advantage of a special raw materials situation. Ethylene glycol from methanol also is dependent on a special raw materials situation which is unlikely to occur in developing countries. Finally, it should be mentioned that methanol consumption for dimethyl terephthalate may be expected to decline in the long run as processes are becoming available for the manufacture of highly pure tercphthalic acid which can be copolymerized to polyester fibres directly, without passing through the intermediate DMT stage.

Technically, methanol is obtained almost entirely by the high-pressure reaction of hydrogen with carbon monoxide, usually over a zinc oxide-chromia-graphite catalyst. The process bears a certain resemblance to ammonia synthesis and, in years past, plants have been used interchangeably for the production of ammonia and methanol. This interchangeability lacks, however, some of the efficiency expected of modern processes for either products and it is no longer practiced on any significant scale.

Technical know-how for methanol synthesis is readily obtainable.

Formaldehyde production accounts for nearly onehalf of methanol consumption. Table 7 shows estimated end-use distribution for this commodity. It should be noted that the first five items in this breakdown have all reached a slow-growth stage in the United States of America and that most of the future growth must come

# TABLE 7. END-USE DISTRIBUTION FOR PORMALDEHYDE (United States, 1963)

				_ ~~						 								Per com
Phenolic resins .																		20.3
Urea resins																		25.2
Melamine resine													÷					7.0
Pentaerythritol														÷	Ì			9.1
Hexamethylene	lei	18	mi	00	•							Ì		÷		Ż		5.5
Other (notably	1			foi		al	del	hy	مٰه				L.	•	Ľ		d.	
polyacetal (re	de.	<b>ie</b> )									_					-	_	17 9

from U-F concentrates and polyacetal resins. U-F concentrates have also potential in emerging economies.

Ammonia and methanol constitute, of course, by far the major outlets for synthesis gas. One other outlet of significance which should be mentioned is the class of oxo alcohols. These are produced by the reaction of olefins (notably heptenes, nonenes and dodecenes) with carbon monoxide and hydrogen in approximately equimolar ratio. Principal cutlet for oxo alcohols is in the production of plasticizers, particularly for polyvinyl chloride. A substantial PVC industry is, therefore, needed in an economy which seeks to upgrade hydrocarbon fractions by the oxo reaction.

#### 4. Acetylene and other methanc uses

Much has been said about the production of acetylene from methane by partial oxidation or by electric arc processes. This conversion accounts today for some 35-40 per cent of all acetylene produced in the U.S. Development of this route to acetylene has been a major technical triumph and an enormous amount of effort has been devoted to it. Long-range, however, this is probably not a very significant factor in the evolution of a petrochemical industry. Developments of the last three or four years threaten to obsolete acetylene in three of its four principal chemical markets, as can be seen from table 8.

Suffice it here to say that acetylene, at a reasonable price (including payout) ranges from 9.5 to 13 cents/lb. and cannot compete with a technology which achieves the same goals from propylene and ethylene at 3-5 cents/lb. In other words, ammoxidation of propylene has already become the bane of acetylene in acrylonitrile production; oxychlorination of ethylene is well on its way in taking over the role of acetylene in vinyl chloride production; and the first two plants are now under construction to produce vinyl acetate from ethylene, acetic acid and air. thus obviating the heretofore established need for acetylene in this synthesis as well.

Several other chemical conversions for methane might be mentioned, though they are minor in terms of total chemical utilization of this hydrocarbon. The more prominent of these "miscellaneous" conversions are:

(1) Chlorination of methane to produce its four chlorinated derivatives. Used mainly as solvents and, to a lesser extent, as chemical intermediates, principal importance among these four products attaches to carbon

TABLE 8. ACETYLENE VS. OLEPENS

Reaction of acotylons with	Yields	Competitive raw materials
HCN	Acrylonitrile	Propylene, ammonia, air
<b>HCI</b>	Vinyl chloride	Ethylene, HCl, air
Acetic acid	Vinyl acetate	Ethylene, acetic acid, air
Acetylene (dimeriza-	-	
tion), HCl	Chloroprene	

TABLE 9. CARBON BLACK

$CH_4 \rightarrow C + 2H_2$ Channel process				8 % of U.S. output
Furnace process (combustion) Furnace process (thermal)	}.		·	92 %

tetrachloride. Note that by-product HCl is formed; its economic disposal is crucial to the costs of methane chlorination.

(2) Reaction between methane and sulphur yields carbon disulphide. The approach is well on its way to displacing conventional production of  $CS_B$  from charcoal and sulfur. Principal use of the product occurs in the manufacture of viscose rayon.

(3) Synthesis of HCN from methane, ammonia and air is an important reaction without a future. The reason is the development of ammoxidation for the synthesis of acrylonitrile, referred to above. Acrylonitrile production is still by far the largest outlet for hydrogen cyanide, however. Another important outlet for HCN is in the synthesis of the nylon intermediate hexamethylene diamine from butadiene.

#### 5. Carbon black

Before completing the discussion of the chemical uses for methane, brief reference must be made to the manufacture of carbon black. In the strictest sense of the word, carbon black — a complex substance which is neither clearly organic nor inorganic — is not a petrochemical. Nevertheless, the importance of this conversion as a consumer of methane is such that a few words about it are here necessary.

Basically, carbon black is produced by the thermal dissociation of hydrocarbon stocks. In the first two processes shown in table 9, the heat needed to achieve this dissociation is provided by incomplete combustion of part of the process stream. The difference between the approaches is that, in the channel process, incomplete combustion takes place as the gas impinges on cooled channel iron while, in the combustion-type furnace process, the conversion is carried out in an empty chamber.

In the third process shown in table 9, thermal black is produced by introducing hydrocarbon feed into a furnace which has previously been preheated by combustion of a gas-air mixture. This process is operated cyclically.

The three processes differ in grade of carbon produced. Furnace production is favoured for its greater efficiency in utilizing hydrocarbons. Thus, furnace processes account for some 92 per cent of the approximately two billion pounds of carbon black produced each year in the United States. It has been estimated that United States production of carbon black in 1962 consumed 133 billion cu.ft. natural gas and 330 million gallons of liquid hydrocarbons. About 95 per cent of carbon black consumption is used by the rubber industry, 2.5 per cent goes to printing inks, the remainder is used in coatings, plastics and paper products. The rubber industry, as main consumer, requires seven major grades and a number of minor grades of carbon black for compounding.

It is obvious that carbon black production makes sense only for a producer capable of selling economically to the rubber industry. Thus, the United States remains the largest producer of carbon black with 68 per cent of total output by the countries with Free Enterprise Economies. Second-largest is the United Kingdom with 9.5 per cent of the world total and France is in third position with the production of approximately 8.5 per cent of the world's carbon black supply.

No other segment of the petrochemical industry is so completely tied to the availability of low-cost hydrocarbon stocks. As a result, essentially all carbon black plants are located directly in the oil and gas fields. Accordingly, carbon black production can become an early stage in the chemical industrialization of gas-rich, developing nations — provided that adequate export markets can be secured in the world's rubber industry. Initial production can even be by the low-investment channel process, despite its lower efficiency and its undesirable air pollution aspects. Carbon black production is not a very impressive way to upgrade the natural gas resource, but is it certainly a better use than flaring.

So far, this paper has dealt chiefly with chemical outlets for methane which is, after all, by far the most important component of natural gas. It should, however, be borne in mind that all of the conversions discussed — with the sole exception of chlorination — can also draw on higher hydrocarbons as feedstock. The reason for methane's important position in this picture is economical, not technical.

TABLE 10. DIRECT CHEMICAL CONVERSION OF C1-C4 PARAFTINE

Parafia	Chemical derivative
Ethane	Bthyl chloride
Propens	
	Perchlorosthylene and carbon tetrachloride Acetaldshyde, formaldshyde, methanol, etc. Acetic acid, methyl ethyl ketone

But natural gas is, of course, a mixture and its ethane, propane and butane content can also be put to efficient use in chemical conversions for which methane is not a suitable feedstock. This covers, above all, the production of olefins which will be examined later in some more detail. But, lest we get the idea that we must go through olefin production or reforming in order to utilize the lower parafins, let table 10 serve as a reminder of some commercial operations in which paraffins are converted directly to substituted organic derivatives.

#### TABLE 11. ETHYLENE CAPACITIES

(Thousand long tons/year)

	Existing	Existing and planned
North America	4,100	5,650
W. Europe	1,950	> 3,700
Japan	500	1,320
Latin America	35	120
All other countries with free enter- prise economies	App. 100	> 200
TOTAL	6,685	10,990

For example, ethane is chlorinated directly to yield ethyl chloride, a raw material for tetraethyl lead production. Propane, subjected to vapour phase nitration, yields a mixture of nitroparaffins, while high-temperature chlorinolysis of propane is one way to make perchloroethylene plus carbon tetrachloride.

Propane and butane can be oxidized non-catalytically in the vapour phase to yield a wide mixture of oxygenated derivatives, among which acetaldehyde, formaldehyde, and methanol are the most important. Two plants using such a process are operated by Celanese Corporation and its Canadian subsidiary. Finally, several processes are now available for the liquid-phase oxidation of butanes and pentanes to acetic acid and methyl ethyl ketone. In most ordinary situations, this is the lowest-cost route to acetic acid.

## 6. Ethylene and its derivatives

For chemical purposes the bulk of ethane and the natural gas liquids are, however, consumed in the production of olefins, which are the broad base on which the organic petrochemical industry has been built.

Ethylene is the bellwether of this industry segment. Present consumption in the United States is slightly above 7 billion pounds per year and it is expected that this demand will increase by 30 per cent during the next five years. Outside the United States, rate of growth is even greater and manufacturing capacity is being expanded accordingly.

As shown in table 11, world-wide ethylene capacity, which is now about 6.7 million tons per year, is slated to reach 11 million tons by 1966. Of the total 1966 capacity, 51 per cent is located in North America and 46 per cent in Western Europe and Japan, leaving only about three per cent for all other regions.

Manufacture of ethylene involves high-temperature, non-catalytic pyrolysis. As shown in table 12, some 40 per cent of current United States production is based on refinery gases and 45 per cent is derived from cracking propane and ethane recovered from natural gas. The remainder draws mainly on liquid hydrocarbons as TABLE 12. SOURCES OF U.S. ETHYLENE

		Per cen
and the second second second second second second second second second second second second second second second		
Refinery grs (direct recovery plu	us conversion of contained	1
ethane and propane)		40
	al gas	

feedstock. In recent years there has been a pronounced growth trend in the role of such liquid feedstocks. The trend is most pronounced in Europe and Japan, where there is an overabundance of light naphtha fractions. However, in the United States, light naphthas and even heavier fractions also serve as feedstocks at major ethylene plants today. A major attraction is the formation of a highly aromatic liquid by-product in the gasoline range which bears some of the manufacturing cost by reason of its blending value. These by-product fractions can be stabilized by several recently developed processes.

Numerous methods are practised to carry out the pyrolysis of saturated hydrocarbons to ethylene. The most widely practised approach involves the use of tubular furnaces. Other methods include cracking by means of highly preheated steam, and the use of pebble heaters, fluid-bed reactors and lead bath reactors.

Yield of ethylene depends on feedstock and depth of cracking which can be adjusted to market requirements. In today's economy, it is, however, usually practical to maximize ethylene formation, in which case the yields shown in table 13 may be expected. It should be noted that substantial formation of by-product propylene occurs in the case of the higher feedstocks, and about one-fifth of the propylene utilized in the United States stems from this source. The remainder can be recovered directly from refinery gases. There is no significant production of propylene for its own sake — propylene formed as by-product in ethylene manufacture and in refining operations more than covers any conceivable requirements.

## TABLE 13. Cg-Cg - OLEPEN FORMATION (At maximum othylone yield)

						Estylene	Propulana						
	k	 	 ( 192. percentage)										
<b>Sthane</b>						80-85	1-2						
						40-45	15-20						
Natural mootine						27-30	12-16						
Crule eil						6-17	6-12						

Ethylene manufacturing economics are, of course, heavily affected by the values assigned to the feedstock and to the co-products. In general, ethane and propane may be considered the ideal feedstock where these components are directly from low-cost natural gas. This is true not only in the gas fields, but also along pipelines. Thus, it is at times feasible to recover an ethane-propane fraction which is brought in, so to speak, piggy-back in a pipeline gas-rich in these fractions.

The choice is less clear between natural gasoline and heavier fractions as feedstock. An interesting evaluation by Kellogg Co. made in 1961 suggests the following general conclusions:

1. Natural gasoline is a preferred feed when ethylene production is limited to 300 million pounds/year or less; and

2. Above 300 million pounds of annual ethylene production, a heavier feed tends to replace natural gasoline as the preferred feed.

Because of the importance of ethylene and propylene as petrochemical derivatives of natural gas, a look should be taken at the principal markets for these basic building blocks of the industry. Obviously, distribution varies between countries in accordance with the degree of industrialization which they have attained. The end-use pattern as it has been determined for the United States is shown in table 14.

TABLE 14. END-USE PATTERN FOR ETHYLENE (United States, 1962)

Percentage	Derivative	Main end-use market
19	Ethyl alcohol	Man-made fibres
25	Ethylene oxide	Automotive
4	Ethyl chloride and ethylene dibromide	Automotive
7	<b>Ethylene dichloride</b>	Plastics, automotive
34	Polyethylene	Plastics
9	Styrene monomer	Plastics
2	Miscellaneous	-
-		

Here is the picture for ethylene. The big consumer is, and will continue to be polyethylene and this is followed by ethylene oxide, raw material for glycol antifreeze and polyester fibres, and finally, by ethyl alcohol which finds its principal outlet in acetaldehyde and acetic acid and, via this route, in cellulose acetate and acetate rayon.

But the pattern is changing fast in the light of new technology. There are new ways to make acstaldehyde and acetic acid which will seriously detract from the alcohol market, and ethylens dichloride will become more important as oxychlorization processes displace acetylene as source of vinyl chloride. Even in styrene, where ethylene serves as one raw material for the intermediate ethyl benzene, competition comes from the direct recovery of this intermediate from a naphtha reformate fraction.

## 7. C<sub>a</sub>-C<sub>4</sub> hydrocarbons

In fact, each of these derivatives of ethylene deserves separate discussion -- and most of them will get it in the course of this conference. For purposes of the present paper, however, attention may be turned to end markets for propylene (see table 15).

TABLE	15.	END-USE	PATTER	N FOR PROPYLENE
		(United	States.	1963)

Percentage of demand	Derivative	Main	end-use market
41	isopropanol and cumene		as solvent for (paints, plastics)
25	Trimer and tetramer	Deterger	3 <b>48</b>
11	Propylene oxide	Plastics polyee	(polyurethanes, sters)
6	Polypropylene	Plastics	
17	Misce, sneous		

Biggest end use is, of course, acetone, regardless of whether it is obtained from propylene via isopropanol or via cumene; in the latter case, phenol is the co-product. Trimer and tetramer are, or rather have been, the secondlargest outlet for propylene, but these branched-chain products are pretty well on the way out in most industrialized countries as straight-chain hydrocarbons must be used in their place in the production of the more biodegradable detergents which are now required.

Propylene oxide is definitely on the way up, impelled largely by its use in fast-growing polyurethanes. Polypropylene, too, is generally considered a "comer" though its rate of growth so far has not come up to earlier expectations. In this connection, attention is also called to important propylene and ethylene markets which are shaping up in the production of ethylene-propylene ternary rubbers. Acrylonitrile, which was not shown among the major propylene derivatives in 1963, has become a significant consumer in recent years.

Butanes are the highest boiling group of hydrocarbons which are normally considered part of the natural gas picture. It has been estimated that the total output of C<sub>4</sub>-hydrocarbons in the United States was 75 billion pounds during 1962. About 70 per cent of this total stemmed from refineries and the remainder was obtained by natural gas processing.

Actually, all but 5 per cent or so of the total was consumed in various fuel applications - in refinery processing and as LPG. The 5 per cent which served as fedstock to petrochemical conversions found its main end market in the synthetic rubber industries, either as

## TABLE 16. CHEMICAL END-USE PATTERN FOR BUTANES (United States, 1962)

											Per cant
Butadiene											70
Alcohois, a											21
lsobutene											6
Other .											3

butadiene or as isobutene. Butadiene alone accounted for 70 per cent of all chemical conversion of both saturated and unsaturated C<sub>4</sub>-hydrocarbons (see table 16).

Among oxygenated derivatives of butane, the biggest factors are secondary n-butanol and its derivative, methyl ethyl ketone, and acetic acid produced by the direct oxidation of butane.

# 8. Sulphur and helium

Sulphur and helium make up the list of important products from natural gas which are not derived from its contained hydrocarbons.

To prevent corrosion in pipeline transmission, it is necessary to scrub out the hydrogen sulphide content of sour gases by one of several alkaline absorption processes. The resulting hydrogen sulphide concentrate is frequently flared in the gas fields, but its conversion to elemental sulphur has risen rapidly during the past decade and it should be practiced wherever some feasible means can be devised for transporting the sulphur to market. Market, in this instance, means primarily the production of sulphuric acid which finds its main end uses in the production of fertilizers, pigments and a variety of other chemicals.

The conversion of hydrogen sulphide to elemental sulphur involves a relatively simple two-step partial oxidation with air. Several processes are commercial and technology is readily obtainable. The technique accounts for some 16 per cent of the present sulphur output in the United States.

Recovery of helium constitutes a special situation which is economically confined to belium-rich natural gases. Helium plants operated in the United States by the Bureau of Mines employ feed gases which have an average helium content ranging from 0.9 to 5.7 per cent.

Though rapid growth is foreseen for helium production during the next decade, this is not a product of serious potential for the developing nations, since they will lack the needed markets. Most of the growth potential is in military outlets - in rockets, missiles, and the atomic field. Even the major civilian outlet for helium calls for an advanced industrial base --- this is the use of helium as inert gaseous shield employed in the welding of titanium, aluminium, magneeium and other speciality metals,

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## B. OUTLOOK

This, then, completes our broad-gauge look at the possibilities which exist in the petrochemical industries as a means of upgrading natural gas resources. Perhaps the outlook can be best summarized by a look at table 17, which is submitted with all the reservations which must be made in such a general and qualitative forecast.

Briefly, what table 17 says is that all economies may expect significant prowth in fertilizer chemicals and in the simpler and low-cost plastics — polyethylens, polyvinyl chloride, and polyetyrene. A synthetic rubber industry based on SBR may form in some of the emerging nations but initial growth of ethylene-propylene rubbers will probably be significant only in the advanced countries. Similarly, the more sophisticated polymers — polyestals, polypropylene and polyurethane resins and acrylic fibros — will, over the next few years, find their growth confined to the advanced economies. But such products as formaldehyde condensate thermoset rusins, point solvents and man-made cellulosic fibres have spont their fast growth rates in the advanced economies. Their production remains a potential growth area in the younger industrial economies.

TABLE 17. POTENTIAL GROWTH ABOAS DI HATULAL GAS PUTBOCHEMICALS

		Advanced contemise			
	.,				
n villages					
Ammonia. La casa a casa a		×	×		
Urea		×	×		
Sulfur	· · · ·		×		
nationie rubbere					
		×	5		
<b>SUR</b>			×		
ahe solvente acciono			×		
and ins					
Polyethylene		×	×		
PVC		×	×		
Polyatyvano		×	×		
Pulypropylano		x			
Polywrethane		×			
Polyassiah		×			
Permaidularia conducation			×		
an-made filtree					
Acrylanivila		×			
Anothe antiputride for estimates			×		

# 3. PETROCHEMICALS FROM NATURAL GAS - THE LACQ EXPERIENCE

Pierre M. Husson, Sociáté nationale des pátroies d'Aquitaine, France

### I. Introduction

Petrochemistry has been defined as a "branch of the organic chemical industry dealing with the development of synthetic chemical products from petroleum derivatives". This definition seems to us a little too narrow.

First, in limiting petrochemistry to the organic field, its importance in the world supply of inorganic products, such as hydrogen, amnonia and sulphur, is overlooked.

Secondly, to speak of petroleum derivatives is to continue to consider petrochemistry as a by-product of the refining industry, under the conditions of the initial development of American petrochemistry. The European experience as well as the American evolution have shown us that in certain cases the fuels become the by-products of petrochemistry.

The definition we finally rotain differs slightly and, going beyond the petroleum and chemistry techniques,

will allow us to consider petrochemistry as a "branch of the industry specialized in the extraction and transformation from petroleum or natural gas or their derivatives, of items intended for the chemical products trade".

Thus, gas can claim the right to be considered as a raw material, on the same footing as petroleum.

Although the chief component of natural gas is methane, the composition of the different deposits varies considerably. Table 1 shows that certain gases are constituted of almost pure methane, e.g. (Romania), and can therefore be transported and utilized without undergoing any processing, others, such as the R'Mel gases are "wet", and contain a considerable quantity of heavy hydrocarbons, which have to be separated. Others still, Lacq, Canada, Iran, contain large quantities of hydrogen sulphide.

According to the case the development of a gas field should provide for special investments, both for the

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Cosmbuses	( <b>****</b> )	Renat R'Nosi (Adgeste)	Carte Manufarr (Bady)	Barnan (Bananta)	Paratar Creat (Canada)	Mosharvan (Nathar- kandar	Dechane (USBR)	(USAR)	Los Angolas (United Simos)	De Soie (United States)	Klaark ( Iraas)
Nydroourbow											
Mothene											
	<b>60.4</b>	83.5	95.9	<b>99.2</b>	77	81.9	98.0	94.3	77.5	97.3	63.6
Silano C <sub>e</sub> lla	2.8	7.8	1.4		3.5	••	• •		i		
Prepara			1.4	-	3.3	2.7	0.7			-	10.3
<b>C, K</b> ,	1.5	2.0	6.4	_	2	6.38	-			-	4.8
Detector C. M.	••							1.7	16.0		
Culling	6.7	6.3	6.2	-0.45	1.5	0.13	- (			-	1.5
<b>C,II</b> ,	6.3	6.3	6.1		6.5		_			_	8.4
<b>C<sub>0</sub> and +</b>	6.)	<b>A.</b> ]	-			0.00	- 1		!		6.2
Valuere											
<b>NA</b>	16.3	-					_		_		10.5
•	9.5	6.2	43	-	4		6.)		6.5	8.4	8.5
N	6.3	6.1	1.0		1	16.0	1.3	1.0		11	

TABLE 1. COMPOSITION OF NATURAL GAS

(Percentage)

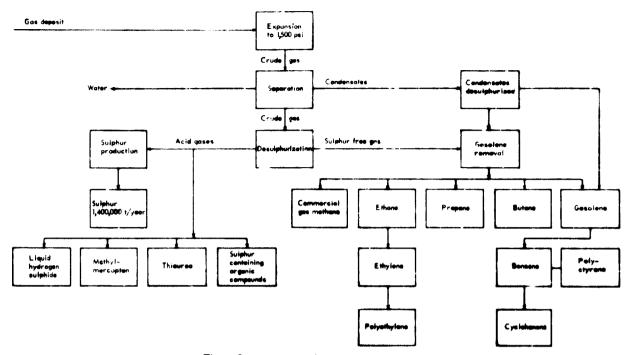


Figure 1. Operations performed at the Lacy Plant

soparating and the production of some constituents requiring special installations.

It is in analysing the development of the Lacq field and the chemical applications of this gas that the problems become clearer and that we can extract certain basic principals, which must not be lost from sight when studying the development of the petrochemical industries in newly expanding countries.

#### II. The emploitation of the Loog fuld

The discovery of the gas deposit goes back to 19 December, 1951, but the real exploitation could not be started before April 1957, for in no other gas deposit previously discovered had there been such an unfavourable combination of circumstances including very high corrosion (the drill pipes were broken and in fragments after a few hours work), high temperature (140° C) and very high pressure at the bottom level --- 9,500 pei at the start of the operations.

Nevertheless, the engineers did not shrink from the difficulties encountered and the initial exploitation was begun with a 1 million/m<sup>0</sup>/day output in 1937 and, four years later, in 1961 the installations absorbed 706 million cft of crude gas daily, set as a working rate. Let us recall that the reserves are estimated at 9,000 milliard eft, of which 7,000 milliard cft are available. An underground storage of 21 milliard cft capacity has been built in the Landes, at 60 kms from Lace, creating at one and the same time a guarantee for the regular working of the factory installations and the supply to the different consumers. The present working rate corresponds to the following annual production:

166 milliard oft of commercial gas 1,400,000 tons of sulphur 350,000 tons of gaseline

130,000 tons of propens and butane,

However, the successful solution of the difficulties of exploitation of the deposit has, since 1961, allowed the Société nationale des pétroles d'Aquitaine (SNPA) to concentrate their efforts on the research and application of the most rational techniques, to valoriae the byproducts from gas development rather than on the gas itself.

### II.1. GAS PROCESSING

The methods of processing the crude gas from Lacq are known (see figure I), and we shall merely indicate that the scrubbing consists in eliminating the acid components H<sub>2</sub>S and CO<sub>3</sub> (about 25 per cent of the rough volume) and in separating the condensable hydrocarbons of very high commercial value:

- Separation of the condensates: at the inist at the plant an expansion system allows recovery of a heavy gaseline, rich in aromatics.
- Desulphurization through amine scrubbing, thus eliminating the hydrogen sulphide and the earbox dismide (figure II).
- Processing of this efficient in the Claus furnesses, to recover the subplue.

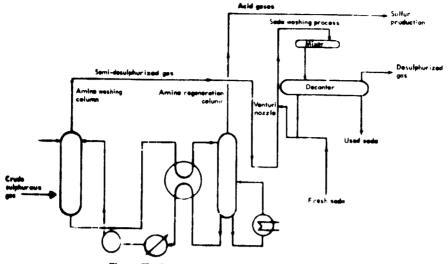


Figure II. Diagram showing amine desulphurisation

# Gasoisse removal through a cascade freezing method or through oil scrubbing in order to recover the other hydrocarbons (figure III, figure IV).

It is at this psolene removal stage that the petrochemical raw material processed by SNPA appears. In fact, the presence of ethane that is technically easy to recover and of oils of a partly aromatic nature, together with the pessibility of their utilization, has allowed us to consider, even before the plant was completed, two lines of petrochemical development: on the one hand ethyleme; on the other hand the aromatic hydrocarbons.

## II.2. CHIMICAL VALORIZATION

# 11.2.a. At the Lacy Plant

It is on the actual gas processing plant that the SNPA has eracted the necessary installations. Propane and

butane have not given way, as yet, to chemical developments, for under the actual conditions of French economy these are far better valued directly and are subject to a classical distribution in steel containers. Besides which butane and propane from Lacq are pure and the refiners, who have at their disposal partly dehydrogenated cracking effluents, are in a far better position to produce synthetic rubber, chiefly butadiene and isobutylene. But the massive delivery of the Sahara production is likely to modify this present economical aspect.

## 2.a.i. Ethylene

The first ethylene unit was erected in 1958 on the second part of the plant that utilizes the refrigeration process, well adapted to the recovery of ethane.

In fact, this process is performed through refrigeration of the gas which has first been cleaned of the sulphides

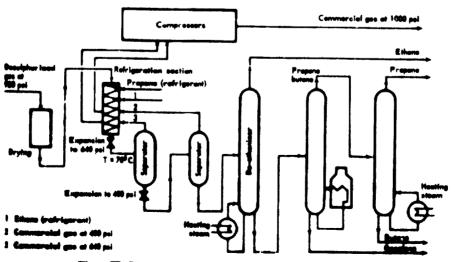


Figure II. Sugram should passible removal to relationation

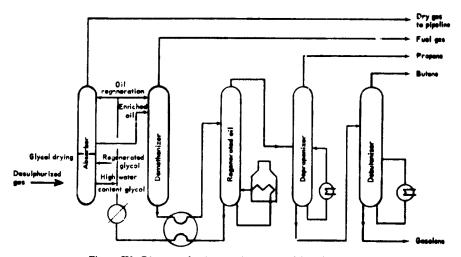


Figure IV. Diagram showing gasoline removal by oil absorption

and carefully dried on silica gel, under a temperature of - 70°C in a series of exchangers under a constant pressure of about 1,000 psi. The separation of gas and the condensable products is carried out by means of two successive volume expansions, first at 640 psi, then 500 si. Of classical conception, this unit produces ethyler. through pyrolysis of the ethane in presence of steam. It has some circuits in common with the gasoline removal unit, as shown on the attached flow-chart (figure V, figure III).

After a soda washing process (elimination of  $CO_{g}$ ) and pressure change to 540 psi, the gases recovered from the cracking are added to the flow coming from the gasoline removal unit.

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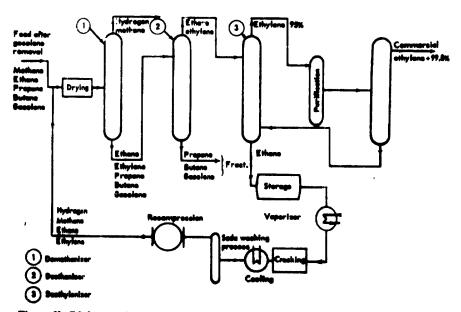
the states

The compound, once dried, feeds the demethanizer, liberating the lighter products such as hydrogen and methane, which are lead towards the commercial gas circuit.

Then the deethanizer separates the ethane-ethylene compound from the condensable hydrocarbons (propane, butane, aromatics) fractionated in the gasoline removal unit.

The deethylenizer, third tower of the assembly, separates the ethane feed from the cracking furnaces and an ethaneethylene compound, to 95 per cent ethylene.

The acetylene is removed from this compound through acetone scrubbing and a final fractionation provides the commercial ethylene of 99.8 per cent minimum purity.



Pignes V. Bilyine production at Long Plant (Int Parind) Bilyine Unit (25,680 tonalyour)

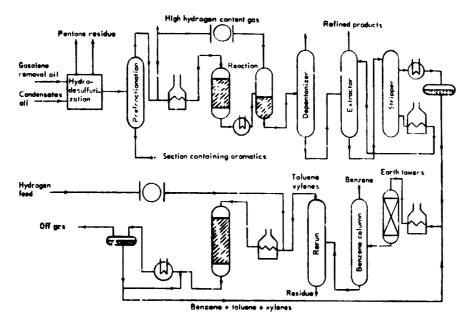


Figure VI. Benzene Unit (70.000 tons/year). Lacq Plant

A pipe-line of 4 km joins the production unit directly to the polymerization unit built at Mont under an agreement with the Ethylene-Plastique Company (24,000 tons/ year capacity).

The separation conditions prescribe an operation at high pressure and low temperature. The power released to obtain the necessary calories reaches 11,000 HP, including the requirements of the gasoline removal unit.

This year the SNPA will produce 20,000 tons of low density polyethylene. But the increased demands for ethylene have made it necessary to construct a second unit of double the working capacity.

This new unit is supplied with ethane by the latterly constructed blocks of the plant where thorough modifications allow a highly efficient gasoline removal. But the absorption process utilized in the new unit does not entail the same case of ethane recovery as the refrigeration process. This unit brings the capacity of ethylene production of the Lacq Plant up to 80,000 tons/year.

Finally, we would like to point out that the first unit is using a process of petroleum origin. The second process has been perfected by the French company Air Liquide and capital investment can be compared with that of the first unit for a production of 1.8 times. This is an outstanding fact which deserves to be emphazised, especially in view of the present survey.

#### 2.a.ii. Benzene

The aromatics from Lacq particularly rich in aromatic hydrocarbons (40 pc, cent) have a double origin:

On one hand the condensates, wich are isolated from the crude gas in the separators of the plant inlet manfolds at the arrival point of the gathering network from the wells. Heavily charged with sulphurized products, these condensates undergo at first an ethanolamine scrubbing in a specialized unit.

On the other hand the gasoline absorption oil, which is lighter and includes paraffin and naphthenes and represents 60 per cent of the whole.

In all, there are produced, every year, 12 million cft of "crude" aromatics creating the raw material which is at the base of the aromatic petrochemistry and bringing into activity a complete plant complex.

The first link of this chain is the benzene unit, of which the diagram is attached herewith and includes four sections (figure VI):

Catalytic reforming;

Extraction;

Dealkylation of the toluenes and xylenes;

Manufacture of hydrogen.

First the aromatics are fractionated. The non-aromatic cut undergoes a reforming process in order to increase the aromatic content. These are then separated by glycol cleaning, followed by a selective extraction of benzene on one hand, and toluene and xylene on the other, a compound which is in turn dealkylated to benzene. This very diversified development requires hydrogen, partially supplied by the reforming unit, the remainder being obtained through cracking of the plant tail gases.

The benzene unit began its activities during the summer 1962. Part of the 70,000 tons/year production is reserved for the state. The rest is used on the spot, as raw material for the manufacture of plastics.

#### 2.a.iii. Plastics

The cyclohexane unit with a 20,000 tons/year capacity, has been in operation since early 1963. Among its numerous applications, cyclohexane is the raw material of Nylon 6. But, taking into account the present situation of the market for this product, the production on the spot is not contemplated for the time being.

The next link of the chain is another unit utilizing simultaneously the benzene and ethylene from the plant in order to manufacture ethylbenzene which through a dehydrogenation process provides the styrene: this unit's capacity is 30,000 tons/year and can be raised to 80,000 tons/year in four years' time. This styrene is partly transformed in the plant for the production of 12,000 tons/ year of polystyrene, whereas the production of styrenic copolymers (AS-ABS) is being considered with a view to production on an industrial scale.

## 2.a.iv. Thiochemistry

The SNPA has finally developed at Lacq the thiochemistry or organic sulphur chemistry, also originating at the gas field. We would like to mention the two specialized units (1,000 tons/year each).

Methyl mercaptan, utilized mainly for cattle feed.

Tiourea used for wood processing and for the stiffening of nylon fabrics.

Other small units supply already or will supply several other derivatives, such as weed killers for agriculture, vulcanization products, etc.

Through this brief survey we have tried to show how the SNPA, by the best utilization of the available resources has brought into value the maximum of production. To achieve this, the company has grafted on the gas processing plant line a number of installations, which, by a diversified chain, allow a range from crude gas to plastics. Let us recall, just to fix ideas, that the complex thus developed employs more than 3,000 persons and represents, drilling section included, a capital investment reaching 1.5 milliard frances (over \$U\$ 300 million).

#### 11.2.b. Pardies Chemical Complex

Apart from SNPA's petrochemical facilities proper. the development of the Lacq deposit has given rise, a few kilometres further away, to a vast industrial complex known under the name "Pardies Chemical Complex".

The attached diagram indicates the general structure of this complex, as well as its productions. The core is constituted by Aquitaine-chimie, created in collaboration with the important French Chemical Companies: Onia, Pechiney, Saint-Gobain and Pierrefitte (figure VII).

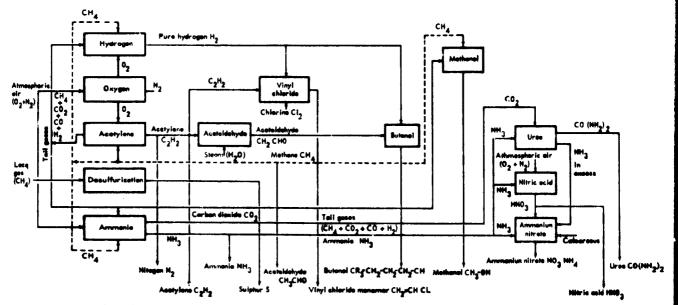
SNPA has accepted a contract for the daily supply of 21,000,000 c.ft. of scrubbed gas, which is utilized in the complex simultaneously as a raw material and as a source of energy. However, it is worth mentioning that the electric current is supplied cheaply by the Artix Electricity Works, fed themselves on gas, supplying, in addition to this complex, the Pechiney Electrolytic Aluminia Processing Plant at Nogueres.

The two key-products developed from gas by Aquitainechimie are acetylene and ammonia. Several other companies have risen around this core, utilizing these raw materials for the development of different chemical products, the entirety of which forms a strongly integrated chemical complex.

#### 2.b.i. Acetylene

Acetylene is obtained through cracking and partial combustion of the natural scrubbed gas, utilizing a pyrolysis process used in the Federal Republic of Germany.

The gas preheated at 600°C is mixed with oxygen and sent to burners. The heat produced through combustion provides the necessary energy for the dissociation of the excess methane. After cracking, the gases are cooled quickly and the carbon black removed. These gases are



Pignes VII. Pardies chemical complex, Acutaino chimis, Acetalana, Vinylana, Maila Piant, Mathemaines, Anvious

quenched and sent to a concentration unit, where the separation and scrubbing of the acetylene occurs.

The concentration unit consists of three towers. In the first tower the acetylene is absorbed by a heavy organic solvent (methyl, pyrrolidine) and the tail gases are recovered to be reutilized for the production of ammonia and methanol. In the second tower the acetylene is stripped under atmospheric pressure, and in the third tower the stripping is completed by vacuum, previous to gas holder storage.

The Pardies complex is equipped with 6 burners, of a 14 tons/day acetylene capacity, i.e., normal production of 24,000 tons/year.

The acetylene yield is about 32 per cent, but the production is linked closely to the quantity of oxygen introduced in the compound. A unit of the French company Air Liquide of a 200 t/day nominal capacity supplies this pure oxygen (99 per cent). At Pardies some 100 tons/air are liquefied per hour, amounting to more than 2,000 tons/day.

The product thus processed does not include the impurities of the acetylene derived from calcium carbide, phosphenes and arsines, causing this special alliaceous odour. On the contrary, the acetylene drawn from methane contains only small quantities of superior acetylenic hydrocarbons, as a result it has a rather agreeable smell.

## 2.b.ii. Tail gases

The tail gases, composed of synthesis gas  $(CO + H_g)$ , are processed by Aquitainechimie for ammonia and methanol production. In fact, if we exclude the production, rarely linked with ammonia synthesis, of hydrogen from natural gas by means of total thermal decomposition, all modern processes use an actual synthesis gas, obtained by the transformation of solid, liquid or gaseous fuels and by steam or oxygen reaction.

#### **Ammon**ia

At Pardies, ammonia is obtained by classical synthesis of nitrogen and hydrogen under 5,250 psi, in the presence of a catalyst. Here the US Chemico process is utilized. The hydrogen is drawn from tail gases, obtainable also directly by reforming of the natural gas. The air provides required nitrogen.

The necessity of completely eliminating the carbon monoxide contained in the synthesis gas before feeding the gas to a catalysis furnace calls for a more complex installation.

The unit consists of:

- Two reforming furnaces, able to treat either tail gas or natural gas uncler a pressure of 300 psi.
- A post-combustion furnace into which is fed the air supplying the required nitrogen.
- A shift converter for the reaction

$$CO + H_{IO} \rightarrow CO_{I} + H_{I}$$

A potash scrubbing plant to remove the carbon dioxide. The CO<sub>2</sub> is sent direct to the Azolacq plant for urea production.

- A copper acctate scrubbing unit to remove final traces of carbon monoxide.
- Finally, an important compression unit, a synthesis reactor and a storage sphere of 53,000 cft., i.e., 1,100 tons of ammonia.

The annual capacity of this unit is 65,000 tons.

# Methanol

The acetylenc tail gas is also well adapted to methanol synthesis. Purified, then compressed to 4,500 psi, the carbon monoxide, carbon dioxide and hydrogen mixture is conveyed to the synthesis reactor (100 tons capacity), that produces raw methanol, which is then distilled. The annual capacity is 40,000 tons.

This process has been improved and developed by the French company Kuhlmann. Research is being continued for a methanol synthesis process, direct from natural gas.

# 2.b.iii. Primary derivatives

# Acetaldehyde

Acetalacq, another company of the complex, converts the acetylene provided by Aquitainechimie to acetaldehyde by water action in the presence of a mercurysalt based catalyst, utilizing the process of the French company Rhône-Poulenc.

A dilute aqueous solution is obtained, which is concentrated and rectified, giving thus the final product. Another unit purifies and regenerates the catalytic solutions. One-third of the annual 25,000-ton production is utilized by a nearby company producing butanol.

# Vinyl chloride

By adding hydrochloric acid, the acetylene allows the manufacture of vinyl chloride monomer, the combination of these two products is also brought about in the presence of a mercury-salt based catalyst.

The acid necessary to the reaction is produced in the plant, by direct reaction of the chlorine on hydrogen, obtained in quartz burners.

The industrial complex has been erected in conformity with the Pechiney-Saint-Gobain processes.

It consists of: a chlorine storage facility, two hydrochloric acid burners, four synthesis converters, a monomer distillation unit, a storage sphere.

The capacity reaches 2,000 tons/month.

# 2.b.iv. Secondary derivatives

#### Butanol

In the framework of the Pardies complex, les Usines de Melle Co. operate a unit for the production of butyl alcohol (butanol). Supplies to the works are guaranteed by the neighbouring companies: Acetalacq provides acetaldehyde and Aquitainechimie hydrogen.

The development passes through different stages: first, condensation to aldol; secondly, dehydratation leading to crotonaldehyde; and thirdly, hydrogenation to obtain butanol.

The production capacity is 10,000 tons/year.

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# Ammonia derivatives

We have seen that Aquitainechimic produced ammonia from the tail gases of the acetylene production.

The transformation of the greater part of this ammonia is operated by the company Azolacq, processing essentially nitric acid, ammonium nitrate and urea.

The nitric acid is obtained by a Pierrefitte process: catalytic oxidation of the ammonia on a platinum sheet and absorption under pressure of the nitrous gases thus produced.

This acid is utilized in the plant itself for the production of ammonium nitrate by simple ammonia addition. The obtained concentrated solution is pulverized in the upper part of a granulation tower, according to a process perfected by Onia. The capacity is nearly 200,000 tons/year.

Urea production is performed in an autoclave under a pressure of 3,000 psi and a temperature of 180°C. The ammonia and carbon dioxide supplied by Aquitainechimie are driven out, urea being obtained by condensation. The production capacity is 40,000 tons/year.

The importance of this industrial plant designed especially for the chemical utilization of gas and in particular of the methane gas is obvious. This complex, grouping six different companies, could only be realized by calling upon the technical and financial means of the most important French chemical companies. To give a more precise idea. let us say that the capital investments add up to more than 350 million francs (about \$80 million) for a plant employing 800 persons and having a turnover of 130 million francs. Furthermore, this complex appears to have reached its optimum size, beyond which it does not seem desirable to go. For too close interdependence of a large number of different productions may present serious operating difficulties causing even the shutdown of the complex, if any one of the productions could not be carried out.

#### 11.2.c. Smoke treatment

In ending this chapter, we think it advisable to say a few words about a recent activity at Lacq: the handling of the smoke from the factory, yielding a new production, that of sulphuric acid.

The average yield of the sulphur units reaches 96 per cent, thus the Lacq plant throws out some 60,000 tons/year of sulphur into the atmosphere, mainly in the form of SO<sub>3</sub>. Although the concentration is very low, the advantage of smoke treatment was a double one:

- To reduce the atmospheric pollution, which is a serious problem already known in numerous other places, and especially when a gas deposit happens to be subhurous;
- To recover the value of the sulphur, which up to now was lost.

But, SO<sub>a</sub> and  $H_{s}S$  are found dissolved in large volumes of industrial gas at very low pressure. This condition increases accordingly the capital investments required and the normal depreciation of such a unit calls for a high production. On the other hand, the notion of financial return might appear to be beside the point when it is a

question of public health and an appreciable decrease of the atmospheric pollution.

The studies carried out indicate that the production of sulphuric acid from industrial smoke would be all the more interesting if the market for this product showed good prospects of continuous development. This production also has the advantage of needing no other raw materials, whilst no by-product is given off that might be difficult to dispose of.

The smoke-processing unit has a production capacity of 100,000 tons/year of  $H_3SO_4$  sent directly by container trucks of 60 tons to the fertilizer plant at Bayonne. This solution guarantees a regular output, enabling the transportation costs to be lowered without competing with the sulphur customers of the SNPA.

# 111. Additions to the general theme

#### 111.1. SYNTHESIS

We have just briefly analysed one of the recent achievements of the French chemical industry, the aim of which is to give a maximum value to the sulphurous gas deposit discovered in south-eastern France.

The whole effect of this achievment spread around Lacq is the result of a common effort between SNPA and the chief French chemical companies. We have examined successively the three "sectors" in which this chemical activity took place: recovering of the value of the by-products from gas processing; actual gas chemistry; and industrial smoke processing.

Taking into account the objective of this Conference, the first two activities are of more interest to us. They confirm that numerous petrochemical products can, under good conditions, be extracted from natural gas, making possible, for instance, the production of ammonia and methanol at a cost price far lower than that from coke which was used to produce synthesis gas in the past.

The example of Aquitainechimie shows to what extent the manufacture of a primary product used by several different companies can be concentrated: thus at Lacq acetylene, ammonia and ethylene, which are among the most important primary petrochemical products, are produced in bulk economical tonnages and distributed to local consumers having their plants in the neighbourhood.

Of course, creating such an organization was not easy. The capital expense involved, the importance of which was previously mentioned, the complexity of the techniques, the commercial and industrial know-how needed, called for a collective grouping of this kind, in order to ensure the complete valorization of the Lacq deposit.

#### III.2. UTILIZATION OF THE NATURAL GAS

It was intentional that we did not emphasize the other aspects of its exploitation. However, the fact that the greater part of this gas is utilized as a source of energy should be kept in mind. More than 6,000 kms of pipeline iced the gas across the country, whilst 50,000 km of distribution network, at medium or low pressure, supply the consumer. These gas sales are important as they represent an appreciable part of the company's resources.

In the immediate neighbourhood of the gas field is built the Artix Electricity Works, where gas feeds three generating groups of 125,000 kW each. Pechiney and Ugine each own one of the generating groups to supply their nearby plants at Lannemezan and Nogueres. Let us also mention that the Pechiney plant at Nogueres, with a yearly output of 90,000 tons of aluminium, is the most important in Europe.

In fact, one should not lose sight of the fact that the petrochemical developments do not constitute the chief part of the actual utilization of natural gas, which vary according to the different countries, as indicated below:

T	A	BL	æ	2

· · · · · · · · · · · · · · · · · · ·	France	Italy	USSR	Romenia
Industrial uses	25	64	36	41
Thermal plants.	31	12	21	21
Chemical synthesis	18	7	10	10
Domestic uses.	23	10	24	26
Miscellaneous	3			20

But, these figures should be utilized with a great deal of care: for instance, in the case of chemical synthesis, which is our particular preoccupation, it is often difficult to differentiate between the amount of gas actually used as raw material and that consumed by the chemists as a source of energy. However, the use of natural gas in the chemical industry is maintained at about 10 per cent. This is a relatively high figure, taking into consideration that the corresponding percentage in the case of the petroleum does not exceed 2 per cent.

One of the most difficult elements of the problem, however, especially as applied to countries with but little industrialization, is how to utilize, in the most profit carning way, the remaining 90 per cent of gas.

# 111.3. THE EXAMPLE OF THE SAHARA

The Hassi R'mel deposit, with a 7,000 billion \* cft reserve, is one of the world's most important. Like the Khark deposit, its main feature is a very high ethane content (+ 7 per cent) and a very low butane content (0.8 per cent), and these important factors affect its chemical utilization (table I).

The development of the deposit is closely linked to transportation, whereas its valorization depends on the exportation conditions.

Surveys are being carried out, chiefly by the SNPA, for the valorization of the liquefiable gases. One difficulty became evident immediately: the low butane content. The quantity required for the operation of a profitable

\* 1 billion - 1 thousand million.

butadiene unit was not compatible with the anticipated exploitation rate of the deposit.

Consequently, the initial project was modified and a contribution of liquefied gases from Hassi-Messaoud was considered. But already the economical conditions of the initial project were altered.

Two points were then studied: transportation of the balance of gas from Hassi-Messaoud; and the construction of an industrial unit producing butadiene, isoprene, ethylene, and propylene.

Indeed, during these last years, natural gas has played an important role in the industrial expansion of France, placing the country among the world's largest producers.

On the other hand, the immense effort put forth in less than ten years and the great technical achievements made, both in the gas extraction and in the chemical industry built around this new raw material, puts France in the first rank of experts on these questions.

# IV. Conclusion --- technical and economic

Technical considerations alone are not enough to settle the difficult industrial problems arising in countries on the threshold of industrialization and we are well aware of this fact. Technical achievements can rarely bear fruits without certain economic and social preliminaries.

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To have important raw material resources at one's disposal is certainly a great asset. However, one must be able to develop and value them in the most rational manner. In most cases, the technical possibilities exist and their holders are surely ready to let these countries benefit. That very important natural gas resources are actually burned on the flare bleeder, which means definitely lost, might seem abnormal, even scandalous to ill-informed persons.

Yet everybody knows the calculations which bring the cost price of the raw material back to zero. However, taking into account the disproportion between other factors, even this assumption is insufficient to obtain a competitive cost price for the finished products. Finally, apart from this cost price, a serious problem of the domestic market comes into being, which, whether it is local, national or regional is, in any case, essential for the absorption of an important part of the production under consideration.

Here, however, we come across general financial and economic considerations, which even if they go beyond the framework of our particular account will certainly be one of the main preoccupations of the Conference. We hope that this modest study, the aim of which it is to show the very real achievements of the Société nationale des pétroles d'Aquitaine at Lacq will contribute to the better understanding of the petrochemical possibilities of natural gas, without forgetting that in addition to the technical problems, which are relatively easy to tackle, some far stricter limits exist, imposed by the notions of profit and outlet.

# 4. USE OF NATURAL GAS AND NATURAL GAS LIQUIDS AS PETROCHEMICAL FEEDSTOCK

# B. L. Bates and R. G. Boatright, Phillips Petroleum Company, United States of America

#### **INTRODUCTION**

The chemical industry is based upon the atoms of the naturally occurring elements. Science has cmulated nature in rearranging these atoms in myriads of combinations and structures to produce products as diverse as synthetic fibres and medicines.

What do we mean by the term "petrochemicals"? The dictionary definition is "a chemical isolated from petroleum or natural gas or a derivative produced from such a substance by chemical reaction". It has been our experience that few informed people agree entirely, and some differ widely, as to what commodities should be called petrochemicals. Are compounds petrochemicals because of their origin, their use, or the process by which they are made? For example, helium is extracted from some natural gas: it is an element, not an organic chemical, and perhaps not a petrochemical, yet it is isolated from natural gas by complex means, and a number of new, large plants have been built in the United States of America to extract helium and sell it to the Government.

Next, what are the building blocks for petrochemicals?

Today, most petrochemicals are derived from those portions of crude oil, natural gas, and natural gas liquids not used in more conventional products such as motor fuel and heating oils. The carbon and the hydrogen so obtained are often combined with other elements such as oxygen, sulfur, nitrogen, chlorine, and fluorine to produce useful and novel substances.

Ethylene, acetylene, propylene, butylenes and butadiene, all composed of carbon and hydrogen, are among the most important reaction materials which are made from petroleum or natural gas. They in turn become building blocks in the making of literally hundreds of new materials which contribute to the making of numerous other products. Some of the most important of these are the so-called high polymers --- plastics and synthetic elastomers. One multi-billion pound per year example is ethylene, made into such diverse products as ethyl alcohol, ethanolamines, ethylene glycol, and trichloroethylene, and into polyethylene, a solid thermoplastic material composed of many linked ethylene molecules. Polyethylene, in turn, is used in a variety of consumer products: in film form, it is a packaging material; in filament form, it is used in fabrics or rope; extruded and blown, it makes plastic bottles; injection moulded, it makes toys, machine parts, and containers.

Thus the uses of petrochemicals are varied and numerous. Besides plastics, they go into antifreeze, aspirin, sulfa drugs, synthetic fibres, nitrogen fertilizers, synthetic rubber, detergents, carbon black, and a wide range of chemicals used in industrial and other chemical processes. One estimate puts the current number of petrochemicalbased consumer products at more than 2,500.

The petrochemical field is large and the markets are growing.

#### **RECENT COMMERCIAL DEVELOPMENTS**

It is important for those having responsibility for planning petrochemical projects to realize that natural gas and liquid products extracted from natural gas are now articles of world-wide commerce. All planning in regard to uses of petroleum energy and petroleum feedstocks should properly take this fact into account. Advances over the past few years in technology, materials of construction, and ocean transport now permit the economic distribution of these products to all of the countries of the globe. Some of these recent activities are:

1. Natural gas liquefaction operations are well proved. The helium conservation programme of the United States Government resulted in the large-scale commercial application of new cryogenic processes and metallurgical developments. Five huge plants in the south-western part of the United States designed, constructed, and operated by private industry are liquefying about 2 billion cubic feet per day of natural gas in the course of recovering the contained helium.

2. Commercial delivery of liquefied natural gas from western Algeria to the United Kingdom was scheduled to commence prior to this Conference. This project incorporates refrigerated tankers and a plant at Arzew designed to liquefy 150 million cfd on natural gas.

3. Over the past two years there has been commercial shipment of propane and butane from the Middle East to Japan in refrigerated tankers.

4. The refrigerated tanker, the "Paul Endacott", with propane cargo capacity of 172,000 barrels, was commissioned earlier this year under long-term charter to our company and has completed several round trips between the Middle East and Japan. Within a few weeks the Paul Endacott will start carrying propane on a regular basis from the United States Gulf Coast to the United Kingdom. The history of the petroleum industry tclls us that these pioneering efforts will shortly become commonplace. Crude oil, by its sheer volume, will continue to be the dominant raw petroleum product. However, it will be found in world operations, as it has been in the United States, that natural gas and its versatile liquid products will find favour in many particular applications.

The producing countries of the world will be looking to external markets in order to realize the full potential of these products in their national economy. Internal uses — which offer most promising opportunities for industrial development — may frequently absorb only a small part of available supply. For example, to supply the Middle East producing countries with the same amount of nitrogen fertilizer *per capita* as is used in the United States would require less than 4 per cent of their surplus natural gas. Therefo z, non-producing countries will also have a broad spectrum of petroleum raw materials to consider in the development of their industries.

# DEFINITION OF NATURAL GAS LIQUIDS

In general, natural gas liquids may be divided into two broad categories: (1) the pentanes and heavier fraction, which is commonly called debutanized natural gasoline, and (2) the butanes and lighter components, which are classified broadly as liquefied petroleum gas or LP-gas.

The composition of debutanized natural gasoline will vary somewhat from field to field, depending upon the character of the hydrocarbon reservoir. But in broad terms it consists of about 55 per cent pentanes, 25 per cent hexanes and C<sub>e</sub> ring compounds, 15 per cent heptanes and C<sub>e</sub> ring compounds, and 5 per cent C<sub>e</sub> hydrocarbons. The gravity is about 80° API and vapour pressure in the range of 11 to 12 #RVP. The natural gasoline of commerce usually is defined primarily by the maximum vapour pressure. Thus we may have 14# natural gasoline, which normally will contain about 5 per cent butanes, on up to 26# natural gasoline, which normally will contain about 1/3 butanes.

Liquefied petroleum gas products are normal butane, isobutane, propane, ethane, and certain mixtures of the foregoing products. Thus mixed butanes, butane-propane mixtures, and propane-ethane mixtures are common articles of commerce. Industry specifications are well established for propane, butane, and butane-propane mixtures (attached as annex is an excerpt of the Natural Gas Processors Association Publication 2140-62 covering definition and specifications for liquefied petroleum gas). Specifications for normal butane, isobutane, ethane, and propane-ethane mixtures are set by agreement between buyer and seller.

#### INDUSTRY HISTORY IN THE UNITED STATES

A brief review of the history of the natural gas processing industry in the United States may give some insight into what the future has in store. The natural gas and natural gas liquids industry had a very humble origin. In the early days of the oil fields, crude oil was the only product wanted. The associated natural gas could be used to a limited extent in lease operations and by adjacent communities for street illumination and domestic purposes. But gas supply in flush pools far exceeded local market requirements. It was early found that hydrocarbon liquids were formed when natural gas was cooled, and the first operations for production of gas liquids consisted simply of compressing the gas and passing it through pipe coils submerged in an adjacent creek. The captured liquids, when weathered to atmospheric pressure, found favour as a component of motor gasoline to power the automobiles which were then appearing on the American scene.

In 1911, United States production of natural gas liquids was 500 B/D. Increasing motor gasoline markets spurred technological advances for extracting liquids from natural gas, and by 1925 production had been expanded to 14,000 B/D. This product, called "natural gasoline", was used exclusively in motor-fuel blending. At about this time the technology of fractionation was introduced, and instead of weathering the extracted liquids to acceptable vapour pressure, the lighter liquids could be removed selectively and produced as a fractionator overhead product. Thus the liquefied petroleum gas industry was born. Records show that the LP-gas market in 1925 was a mere 1,000 gallons per day.

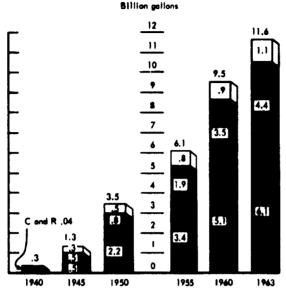
From 1925 onward the production of natural gasoline and UP-gas continued at a rapidly accelerated rate. Currently United States production of natural gas liquids is in the order of 1,200,000 barrels daily, or about 1/7 of total United States production of all petroleum liquids.

In the meantime, the natural gas industry continued to develop. In 1935 marketed production of natural gas was about 6 billion cfd, all of which was for local and regional markets. However, technological developments in pipeline construction and conditioning of natural gas were beginning to make possible the economic transport of gas from remote reservoirs a thousand miles and more into all parts of the country. Today, marketed production of natural gas in the United States exceeds 42 billion cfd. It now supplies 30 per cent of all energy consumed in the country. Natural gas transmission and distribution are now the country's sixth largest industry, with a total investment of \$26 billion.

#### UNITED STATES MARKETS

The energy market has been the dominant outlet for natural gas. Less than 6 per cent of the United States marketed production is used in the manufacture of chemicals. Natural gas liquids also have been used largely in energy markets, although petrochemical use has been increasing. Today about 25 per cent of total natural gas liquids are used for petrochemical feedstocks. Substantially all of this volume is made up of the liquefied petroleum gases (see figure, LP-gas industry sales in the United States). About 40 per cent of the marketed production of LP-gas is used in petrochemical





LP-gas industry sales growth in the United States

manufacture. About the same amount goes into heatingfuel markets. A little under 10 per cent is used as such to fuel internal combustion engines, and the remaining 10 per cent goes to miscellaneous industrial uses. Substantially all of the natural gasoline, which comprises about 40 per cent of total natural gas liquids production, is used in the manufacture of motor gasoline.

#### WORLD MARKETS

Important differences exist between United States and world markets for natural gas liquids. Primarily this results from the relative values placed on the motor fuel portion of the petroleum barrel. The United States places a premium value on motor fuel boiling range components, whereas other countries having little or no natural gas and relatively low motor fuel demand regard fuel oil and diesel oil as primary products. Thus light naphtha has become a by-product in refinery operations and is the most available feedstock for their chemical plants.

The entry of natural gas into the European energy picture can be expected to have an effect on the future outlook for petroleum naphtha in petrochemical operations. The discovery of huge natural gas reserves in the Netherlands has caused all of northern Europe to re-assess natural gas as a possible major addition to their energy needs. The current exploration activity in the North Sea could uncover additional large gas reserves. With less dependence on fuel oil to supply increasing energy needs and more dependence on gasoline range components to supply increasing motor fuel demands, "there", will be an increasing tendency for the refiner to place a higher value on naphtha. Natural gasoline, the pentane and heavier fraction of natural gas liquids, falls into the same category as light naphtha. Its predominant use in present world markets can be expected to be in the manufacture of petrochemicals. On the other hand, LP-gas, because of its versatile applications in the field of energy, will be channelled preferentially into energy markets except for those petrochemical operations in which it has premium value.

#### PETROCHEMICAL FEEDSTOCKS

Above we have emphasized two major characteristics common to the full range of petrochemical feedstock hydrocarbons, natural gas through naphtha. The first is that they can be made available anywhere in the world. The second is that, as petrochemical feedstocks, they will be produced by facilities which have as their primary purpose the production of energy fuels. Thus their value will be strongly influenced or set by the value of energy fuels but their use will be determined by their relative cost and value to the petrochemical producer. As we shall see, many factors enter into this use value.

Let us look now at some of the major primary petrochemicals, what feedstocks can be used, and the effects of feedstock.

Nitrogen fertilizers are a key factor in upgrading the efficiency and productivity of the agricultural section of any economy. Synthetic nitrogen fertilizers are based on ammonia which may be produced from any of the range of feedstocks considered. In this process, of course, it is the hydrogen part of the hydrocarbon which is desired and the carbon portion must be removed (admittedly after contributing to hydrogen production through the carbon monoxide-steam shift reaction). For this and other technological reasons, methane is a very desirable feedstock and is dominant in the United States. This will be the case in other countries where natural gas is produced or can be delivered cheaply by pipeline.

In other parts of the world, with natural gas unavailable or prohibitively expensive, heavier stocks such as naphtha have been used. However, heavier feedstocks impose a higher plant investment. Thus the familiar problem of belancing continuing operating costs against the cost or payout or return on initial capital investment is introduced. This value of capital as well as the relative cost of various hydrocarbons may vary in every case considered. Comments similar to these on ammonia apply to the closely related methanol industry.

Because of its tremendous world volume and versatility, ethylene is usually among the first petrochemicals considered for new industry. However, it should be pointed out that in few other industries is the effect of plant capacity so influential on plant and product costs. Thus a viable ethylene-based industry is inherently large and expensive. Also cracking plants for ethylene production supply a variety of by-products, some of which may be used in other petrochemical operations. The success of the petrochemical venture hinges in large part on finding profitable outlets for the by-product materials. The choice of ethylene feedstock therefore depends not only on its cost but also upon yield of respective byproducts and the values which can be placed upon these materials.

Typically, the yield of ethylene increases with decreasing molecular weight of the cracking feedstock. For example, high severity cracking of light naphtha will yield in the range of 25 per cent to 30 per cent ethylene, whereas propane will yield about 40 per cent and ethane about 70 per cent. Plant investment and operating costs decrease to some extent with increased yield because of the lower total amount of feed and cracked products required to be processed.

Also the ratio of propylene to ethylene decreases with decreasing molecular weight. Thus with naphtha about 2/3 of a pound of propylene is produced for each pound of ethylene. This often results in surplus propylene over and above local petrochemical requirement. With propane a little over 1/3 pound propylene is produced for each pound of ethylene. With ethane the production of propylene is less than 1/20 of the ethylene production.

In this connexion it is of interest that our company has recently developed the Triolefin Process to convert propylene into ethylene and normal butylene efficiently. This adds a new degree of freedom for the ethylene producer.

Another important factor in feedstock selection is the volume of gasoline range by-product material and its value. Many naphtha cracking operations are integrated with crude oil refining processes and this gasoline fraction, which may run 25 per cent or more of the original charge stock, can be returned at premium value for use in motor fuel blending. With propane the pentanes and heavier fraction is about 10 per cent of the charge stock and with ethane less than 5 per cent of the charge. In the United States very little of this product from ethane and propane cracking is used in motor fuel because of its premium value in benzene recovery operations and in the production of petroleum resins.

In all cracking operations for the production of ethylene a substantial volume of a residue gas comprised of hydrogen and methane is recovered. In many cases the volume will be large enough to support an economic size ammonia plant without reliance on supplementary feedstock. When not used in this manner, it can supplement the cracking plant fuel.

Another important by-product chemical from cracking operations is butadiene. It will usually be found economic to install butadiene recovery facilities in conjunction with a large ethylene plant. If the market for butadiene exceeds the by-product supply, it can be produced by the catalytic dehydrogenation of normal butane. In the United States nearly half of total butadiene production is based on normal butane, with the remainder from dehydrogenation of refinery butylene and by-product recovery from cracking operations.

#### CONCLUSIONS

1. Natural gas liquids products are now available on a world-wide basis.

2. Plans for specific petrochemical projects should include a careful examination of the value of these products as feedstocks.

3. The ability to start with natural gas liquids lessens the dependence of the petrochemical industry on crude oil refining operations. This can lead to petrochemical manufacture in locations where petroleum refining does not exist.

4. Natural gasoline, the pentanes and heavier portion of natural gas liquids, is in effect a high API gravity petroleum naphtha and may prove superior in certain petrochemical projects to the conventional light naphtha obtained from crucie oil.

5. Ethane when used as a source of ethylene yields relatively little by-products which may be a basic incentive when the operation is remote to the market for such by-products.

6. Petrochemical use of propane and butanes will meet with strong competition from the energy market. Yet under certain conditions of by-products uses and values, they may be found superior to other petroleum feedstocks.

In closing, the petrochemical industry is and has been an important factor in bringing to the customer a wide choice of products, and because of this it promises to be a continuing force in the years ahead. Consumers, distributors, and producers and processors of energy and of hydrocarbons will continue to benefit from it.

#### Annez

## NGPA LIQUEFIED PETROLEUM (AS DEFINITIONS AND SPECIFICATIONS •

#### Effective not later than 1 January 1963

#### COMMERCIAL PROPANE

Commercial propane shall be a hydrocarbon product composed predominantly of propane and/or propylene and shall conform to the following specifications :

#### Vapour pressure

The vapour pressure at 100 F as determined by NGPA LPG Vapour Pressure Test shall not be more than 200 pounds per square inch gauge pressure.

#### 95 per cent beiling peint

The temperature at which 95 per cent of volume of the product has evaporated shall be -37 F or lower when corrected to a barometric pressure of 760 mm Hg., as determined by the NGPA Weathering Test for Lignafied Petroleum Gases.

#### Resider

The product shall pass the non-volatile recidue test and shall pass the oil ring test --- or the as determined by the NGPA. Method for Determining Residues in Liquefled Petroleum Gases.

#### Polatile suffer

The unstanched product shall not contain velocile suffer in encome of Afreen grains per hundred custic feet a determined by NGPA Velocile Suffer Text.

Encorpted from NGPA Publication 2146-62 Natural Cas Processors Association, 429 Kennedy Bidg., Tutes 3, Oblahams.

#### Corrosive compounds

The product shall cause no more discolouration to a polished copper test strip when such product is subjected to the NGPA LPG Corrosion Test than the discolouration of Standard copper strip Classification 1, as described in ASTM Method D 130-56, table 1, Copper Strip Corrosion by Petroleum Products.

#### Drymess

The product shall be dry as determined by the NGPA Propane Dryness Test (Cobalt Bromide Test).

#### COMMERCIAL BUTANE

Commercial butane shall be a hydrocarbon product composed predominantly of butanes and or butylenes and shall conform to the following specifications :

#### Vapour pressure

The vapour pressure at 100 F as determined by NGPA LPG Vapour Pressure Test shall not be more than 70 pounds per square inch gauge pressure.

#### 95 per cent boiling point

The temperature at which 95 per cent of volume of the product has evaporated shall be 36 F or lower when corrected to a barometric pressure of 760 mm Hg., as determined by the NGPA Weathering. Test for Liquelled Petroleum Gases.

#### Vulatile sulfur

The unstenched product shall not contain volatile sulfur in excess of fifteen grains per hundred cubic feet as determined by NGPA. Volatile Sulfur Test.

#### Corrosive compounds

The product shall cause no more discolouration to a polished copper test strip when such product is subjected to the NGPA LPG Corrosion Test than the discolouration of Standard copper strip Classification 1, as described in ASTM Method D 130-56, table 1, Copper Strip Corrosion by Petroleum Products.

#### Dryness

The product shall not contain free, entrained water.

#### BUTANE-PROPANE MEXTURES

Butans-propane mixtures shall be hydroserbon products composed predominantly of mixtures of butanes and/or butylenes with prepane and/or propylene and shall conform to the fullowing excellections:

#### Vapour pressures

The vapour pressure at 100 F as determined by NGPA LPG Vapour Pressure Test shall not be more than 200 pounds per square instiguings pressure.

#### 95 per cent belling point

The temperature at which 95 per cent of volume of the product has eveporeted shall be 36 F or lower when corrected to a barometric pressure of 760 mm Hg., as determined by the NGPA Westhering Tast for Ligateled Petroleum Gases.

#### Volutile miller

The unstanded product shall not contain volatile suffer in energy of filteen grains per bundred cubic fast as determined by NGPA Volatile Setter Text.

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#### Corrective compounds

The product shall cause no more discolouration to a pollshad copper test strip when such product is subjected to the NGPA LPG Corrosion Test than the discolouration of Standard copper strip Classification 1, as described in ASTM Method D 130-56, table 1, Copper Strip Corrosion by Petroleum Products.

#### Drymene

The product shall not contain free, entrained water

#### **Product designation**

Butane-propane mixtures shall be designated by the vapour preswre at 100 F in pounds per square inch gauge. To comply with the designation the vapour pressure of mixtures shall be within +6 lb .5 Ib of the vapour pressure specified. For example: a product specified as 95 pound LPG shall have a vapour pressure of at last 90 lb but not more than 95 lb, at 100 F.

## PROPANE HD 5

Propane HD 5 shall be a special grade of propane for motor fuel and other uses requiring more restrictive specifications than commercial propane and shall conform to the following specifications:

#### Vapour pressure

The vapour pressure at 100 F as determined by NGPA LPG Vapour Pressure Test shall not be more than 200 pounds per square inch gauge pressure.

#### 95 per cent beiling point

The temperature at which 95 per cent of volume of the product has evaporated shall be -37 F or lower when corrected to a barometric pressure of 760 mm Hg, as determined by NGPA Weathering Test for Liquefed Petroleum Gases.

#### Resider

The product shall pass the non-volatile residue test and shall pass the oil ring test-each as determined by the NGPA Method for Determining Residues in Liqueflet Petroleum Gases.

#### Volatile sulfur

The unstenched product shall not contain volatile suffer in encour of ten grains per hundred cubic feet as determined by the NOPA Volatile Suffer Test.

#### Corrective compounds

The product shall cause no more disseleuration to a palished copper text strip when such product is subjected to the NGPA LPG Corregion Text than the disseleuration of Standard copper strip Causifunction 1, as described in ASTM Muched D-130-56, table 1, Copper Strip Correction by Petroleum Products.

#### Drynna

The product shall be dry as determined by the NGPA Propried Drynam Test (Colorit Bremide Test).

#### Composition

The propylane content of the product chall not encod five liquid volume per cost and the product chall contain a minimum of almsty liquid volume per cost of program.

# 5. NAPHTHA STEAM CRACKING AND UTILIZATION OF ITS PRODUCTS

Shigeru Hayashi and Yoshihiko Hirakawa, Nippon Petrochemicals Co. Ltd., Japan

## 1. INTRODUCTION

Ethylene is one of the most important basic materials for the production of leading petrochemicals, namely, polyethylene, ethylene oxide and glycol, acetaldehyde and acetic acid, styrene, ethylene-propylene rubbei, etc. However, only insufficient quantities of it can be recovered from the refinery cracked gas even in the United States of America, where tremendous cracking capacity exists.

Therefore, in those countries, such as Japan, where only small cracking capacities in the refineries exist and where the availability of wct natural gas and/or refinery gas is limited, ethylene is supplied almost wholely by naphtha cracking excepting the small quantities recovered from coke oven gas. The recovery from coke oven gas, however, has rapidly become uneconomical in competition with naphtha cracking.

We would like to attempt to show how the petrochemical industry in Japan, established on naphtha steam cracking, has endeavoured to maintain a balance between the ethylene production and a full utilization of its products; and how important this is for a country such as Japan where naphtha is the major raw material for the production of ethylene, accompanied by large quantitien of by-products.

# 2. AVAILABILITY OF FEEDETOCKS FOR THE PRODUCTION OF ETHYLENE IN JAPAN

It is estimated that oil requirements for this year will reach about 67 nullion kilo-litres with an annual increase of 27 per cent as has been the case for the past five years; however, it is forecast that the annual rate of increase in the coming four years will be about 14 per cent and that the total requirement will reach 113 million kilolitres in 1968.

Stimulated by such vigorous demand increase, oracle oil distillation capacity in Japan has reached 1,443,400 barrels/day as of 1 January 1964. Japan now has the sesond largest capacity of those countries with free enterprise economics and is surpassed only by the 10,620,000 barrels/day capacity of the United States of America. However, the demand structure of oil products in Japan is very different from that of the United States of America, and is rather similar to that of European countries, especially Italy.

In Japan gasolone consumption 1964 is only 16.9 per cont of the total eil domand, and this figure, it is forecast, will decrease slightly to 16.3 per cent by 1968. On the other hand, the combined consumption of distillate fuel and residual fuel oils this year will reach 68.4 per cent of the total oil demand, whereas, it will climb to 69.2 per cent by 1968. About 85 per cent of the required crude oil depends on imports from the Middle East, and such a demand structure of oil products has produced a surplus supply of naphtha, especially the light straight naphtha whose octane number cannot be upgraded economically by catalytic reforming. On the other hand, the light straight naphtha of Middle East crude is paraffinic and it is a most desirable material for the production of ethylene by steam cracking in the countries where sufficient quantifies of refinery gas and wet natural gas are not available.

The production of natural gas in Japan reached 1,684 million cubic metres in 1963 with a remarkable 31 per cent annual increase rate continuing for the past eleven years since 1952, when the utilization of natural gas for chemicals began. Its consumption for chemical uses, mainly for the production of ammonia and methanol, in 1963 was 70.0 per cent of the total gas consumption as compared with 75.0 per cent in 1962, which was the peak year for chemical consumption. There are, moreover, indications that the production of natural gas in Japan has slackened, and some of the gas chemical producers have begun to use, or are considering using, naphtha as raw material.

The production of natural gas in Japan is practically limited to dry gas, and the supply of wet natural gas is very limited. As a result, light straight naphtha is the most desirable material for the production of ethylene in Japan with respect to improving the oil demand structure and to producing ethylene economically and proficiently.

# 3. TYPICAL YIELD PATTERNS OF INDIVIDUAL PLANTS

In the case of cracking naphtha for the production of othylene, the yield pattern of cracked products varies according to the processes and the operating conditions used. With the enception of one ethylene plant that uses the Société belge d'azote process to co-produce acetylene and ethylene by naphtha flame cracking and one sand cracker based on the Ruhr-Lurgi process, all other ethylene plants in the nine petrochemical complexes in Japan are using naphtha steam cracking process for the production of ethylene. All of the naphtha steam crackers

TABLE I

Plants	•	3	C	D	E
Ethylene	22	20	19	16	19
Propylene *	18	14	17	13	17
C <sub>a</sub> -C <sub>a</sub> fraction	16	12	15	11	15
Cracked nephtha	19	26	15	42	21
Residuel oil	1	9	5	۹.	4
Off-gaa	20	17	27	13	22
Lose	2	2	2	2	1

· Containing more than 90 per cent propylene

use Stone & Webster Engineering Company's process, excepting two, of which one uses the Esso Research & Engineering Company's process and the other the Universal Oil Products Company's process.

Table 1 shows some of the typical yield patterns of the plants based on naphtha steam cracking.

In table 1, the smallest yield of ethylene in plant D results from milder operating conditions, more similar to those of thermal naphtha reforming, and the yield of cracked naphtha, which can be blended to gasoline after simple treating, is the highest. Plant E datum is used for the calculation by industrial Structure Investigation Council for Japanese Government of economics of naphtha steam cracking as it affects that of the whole petrochemical industry.

The data in the table indicate that the more the ethylene yield increases, the more the cracked naphtha yield decreases. Higher ethylene yield is attained by more severe cracking conditions, unless other operating conditions change, and such conditions lead to a higher aromatic content in the cracked naphtha, which is a more valuable feedstock for the extraction of BTX (benzene, toluene and xylenes) than for blending to upgrade the octane number of gasoline.

#### 4. EFFECT OF FEEDSTOCK COMPOSITION ON YIELD PATTERN

The cracking reaction of naphtha to othylone and other products occurs by free radical reaction mechanism. The thermal stability of parafinic hydrocarbons is lower than that of naphthonic and aromatic hydrocarbons. It means that parafinic hydrocarbons are easier to crack than other types of hydrocarbons. Moreover, cyclic hydrocarbons, such as naphthonic and aromatics, tend to produce tarry matters by cracking, and as a result more frequent cleaning of the furnace tubes is required to maintain the efficiency of a plant.

Fortuactoly, the straight naphthe derived from Middle East crude is essentially parafilmic. However, because of material situation and availability, there arise occasions when naphthe rich in naphthonic hydrocarbons such as those derived from Russian crude will have to be used. In table 2, we present only the effect of feedstock composition on yield pattern.

Butadiene is the most valuable product of the cracked products, including ethylene. Butadiene, which is the raw material for the production of such syntuetic rubbers as styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR) and stereo polybutadiene, is contained in the  $C_4$ - $C_6$  fraction of naphtha cracked products. Generally speaking, the amount of butadiene produced is about 3 per cent of feed naphtha charge and about 30 per cent of  $C_4$  fraction, equivalent to about 20 per cent  $C_4$ - $C_6$  fraction, though it tends that there is a greater amount of butadiene produced from naphthenic naphtha than that from the paraffinic one.

In Japan, the butadiene contained in the  $C_4$  fraction from naphtha cracking is recovered, at the present time, exclusively by the cuprous acetate ammonical (CAA) solution process of the Esso Research and Engineering Company.

It is found to be more economical to recover the byproduct butadiene than the butadiene from butane or butene dehydrogenation, not only because the latter produces no valuable by-products but also because the concentration of butadiene in the dehydrogenated products is lower (for example, about 11 per cent for butane dehydrogenation and about 16 per cent for butylene dehydrogenation).

For composition analysis of raw materials and products in naphtha cracking operation, such precise methods as gas chromatography, infrared spectrometer and mass spectrometer are generally used. Gas chromatography is particularly a powerfully weapon for composition analysis. For reference, we have shown in table 3 some typical results obtained by gas chromatography of naphtha feedstock given in table 2.

#### THELP 2

Naphtha dorived from	Middle Bart	Russian
Specific gravity	0.606	0.726
Initial bolling point, "C.	26	32
10 % distillation tomp., "C	46	63
50 % distillation temp., "C	84	116
99 % distillation temp., "C	131	160
End point, "C	t7t	185
Compatition, vol. %		
Parafiniz hydrocarbon	78	
Nephthenic hydroenrhons	19	30
Aromatios hydrocarbons	3	12
Created products, wt. %		
Babylons	21	*
Prepylane *	17	17
CrC, fremien	16	10
Creshed nephthe	17	10
Review	4	4
Oli-gas	23	28
	1	1

· Containing more than 10 per cent propylan...

TABLE	3
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		Middle East	Presian
C,	i-Dutane		
~4	r-Dutane.	· · 1.0 · · 12.3	1.0 3.5
	2,3-Dimethylpropane.	Trace	<b>A</b> 1
C,	i-Pentane		6.1 3.2
	n-Pontane	11.7	4.2
	Cyclopentane	1.0	0.6
	2,2-Dimethylliutane		0.2
	2,3-Dimethylbutane	· · · 1.0	6.3
C,	2-Methylpentane	· · <b>6.3</b>	2.7
	n-Hexane.	· · <b>5.1</b> · · <b>12.7</b>	1.9 4.2
	Methyleyclopentane		2.5
		2.2	1.6
	Tencene	<b>9.8</b>	0.6
	2,2-Dimethylpeniane.	0.2	0.2
	2,4-Dimethylpentane		0.3
	3,3-Dimethylpentene 2,3-Dimethylpentene	0.1	0.1
	3-Methyllenane	· · <b>6.6</b> · · <b>5.4</b>	3.2
С,	n-Plapiana	10.1	3.1 4.7
	1,3-Dimethyleyelepentene.	2.2	2.8
	1,3-Dimethyleyelepentane	. 82	0.2
	Muthylaydohenane	. 2.5	3.6
	Ethylayologontane . Taluane	••• <b>••</b> ••	0.6 2.2
	2.2-Disselbythenane		
	2,4 and 2,5-Dimethylhonane	••••	0.5 0.5
	unhappun	1.0	2.2
	3,4-Dimstightenane	. 11	2.9
~	3-A-Mothylhoptane	. 9.6	1.9
<b>G</b>		. —	5.1
	s-Ostano	. 0.7	4.0
	Bilgispelulunane		0.2 1.5
	Interested and a second s	A 1	0.9
	<b>P. III-Xiyiste</b>		2.3
	C-Xylune	Tree	1.1
	Alighatic isomers	. 6.2	7.3
		. 0.1	4.1
C	Propyllenene .	•	4.2
-	p., m-Billyficiums.	•	8.3
		3 .	1.1
	1,3,5-Trimstiylbunasas.	1	- ii
			1.2
	1,2,3-Trinstigthenene.	.1	8.6
-	Allphaste terrere	•1	6.2
C	n-Busano. C <sub>in</sub> Aromatip.		22
_			6.7
C.,	Allphaite isomers	·) Team	26
•		•••	•••
	Alphalis instance		6.5 6.1
•		-	
	_		

# 5. LOCATION OF PETROCHEMICAL PLANT AS IT AFFECTS UTILIZATION OF BY-PRODUCTS FOR CHEMICAL USES

To attain the highest economical efficiency of a naphtha cracking plant, a complete utilization of by-products must be realized. It is, however, difficult to realize, since they are not produced independently of ethylene, to which the demand operation of the plant must be geared. Therefore, plant location becomes an important factor.

For example, we may take the case of our own company the Nippon Petrochemicals Company, Ltd. (NPCC). The naphtha cracking plant is located in Kawasaki City, which is a centre of Tokyo-Yokohama Industrial Area near Tokyo International Airport (Haneda).

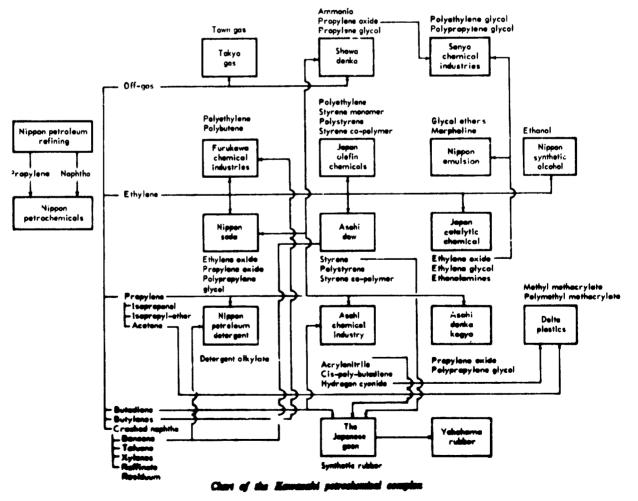
NPCC is a wholly owned subsidiary company of Nippon Oil Company, Ltd. (NOC), which is the largest and the oldest oil company in Japan. NOC, in partnership with California Texas Oil Corp. (CALTEX), established the Nippon Petroleum Refining Company, Ltd. (NPRC). One of its refineries, the Yokohama Refinery, is the major supplier of narhtha and propylene to NPCC, as shown in the flow-chart.

The Kawasaki petrochemical complex, in which many chemical companies are being supplied with basic intermediates from NPCC's naphtha cracking plant, is different from other complexes in Japan. That is, most of the members of the Kawasaki petrochemical complex have no special affiliation nor do they own significant shares of the other member companies. Each member is independent, endeavouring to work in harmony and unity for the common interest of establishing an outstanding petrochemical complex at Kawasaki.

In addition to the arrangements as shown (see below), the Kawasaki complex established a network of mutual utilization of utilities; for example, steam from NPCC to several companies, hydrogen from Asahi Dow to NPCC, nitrogen from Showa Denko to most of the members, joint ownership of seawater intake facilities by NPCC and Furukawa Chemical Industries, and open use of NPCC's jetty for the member companies.

One of the factors which has led to the success of our complex is the proper selection of its location. Kawasaki is located in the centre of the Tokyo-Yokohama industrial area, its importance is not only in the area of the process industries of petrochemical end-products such as plastics concentrated in this part, but also in the largest market for petrochemicals in Japan.

In these circumstances, ethylene from NPCC is used to produce polyethylene, styrene and polystyrene, ethylene oxide and glycol, and ethanol by a number of companies



in the complex. Propylene from NPCC is supplied to produce propylene oxide and glycol, acrylonitrile and detergent alkylate, and it is also used by NPCC to produce isopropanol and acetone. The propylene demand for petrochemicals by the members of the complex, including ourselves, is more than we can supply; so NPCC receives the propylene fraction of catalytic cracked gas from NPRC. When our propylene finds no outlet for petrochemicals, it is supplied to Nippon Petroleum Gas Company, Ltd. (NPGC), another subsidiary company of NOC, for the LPG market. At present, NPGC imports LPG from Saudi Arabia.

Butadiene is, of eourse, supplied to produce many types of synthetic rubbers, but butylenes are supplied to the only company now producing polybutene in Japan. Of the BTX extracted from cracked naphtha, benzene is used to produce styrene and detergent alkylate within the complex.

Among the cracked products, the off-gas, which consists essentially of hydrogen and methane, with or without ethane, is not a prime production of the naphtha cracking operation, but its full utilization has a marked influence on the economics of the plant operation, for its very large quantities as compared with other products generate substantial revenues despite its low selling prices. On the other hand, the naphtha cracking operation requires large amounts of fuel, equivalent to about 15 per cent of feedstock charge. It should naturally be of the lowest value. We are using now one third of off-gas corresponding to about 50 per cent of the total fuel requirement for the purpose.

The remaining fuel requirement for the cracking operation is met by other by-products, which have yet no profitable outlets. A large portion of our off-gas is used for ammonia production and town gas. Ammonia production is a traditional and important business in Japan; however, in the recent years competition with foreign producers has become very keen, and the Japanese producers must find more reasonable and cheap starting materials to begin with. Our clients who are producers of ammonia are constantly exerting pressure on us to reduce the price of off-gas.

On the other hand, town gas business in Japan is a monopoly in the area of business. It has attained a high degree of rationalization by converting the traditional raw material, coal, to oil and natural gas. Tokyo Gas, one of our clients, is the largest gas company in the business and has one of its plants built within 10 kilometers from our plant. Our company and another one located in the same area, which enjoy this advantage for the off-gas outlet because of the location of the plants, are the envy of the remaining seven petrochemical complexes in Japan, which do not enjoy the same advantage.

The second point of importance to be considered with respect to the full utilization of by-products is the use of the propylene fraction as liquified petroleum gas (LPG) for household use. In Japan, LPG has been supplied not only by the refineries and petrochemical plants but also by imports from Middle East. Therefore, the propylene fraction of naphtha cracked products, which was ariginally disposed of has now become a permanent merchandise as LPG instead of being sold as a petrochemical feedstock, as it should be.

# 6. ANNUAL CHANGES IN THE UTILIZATION PATTERN OF CRACKED PRODUCTS FOR CHEMICAL USES IN JAPAN

As ethylene is the main product of naphtha cracking, the eracking capacity should be expanded in accordance with the increasing ethylene demand. A trend in the actual production of ethylene in Japan is shown in table 4.

The production figure shows a 90 per cent annual increase, on an average, during the past five years, and even the increase in 1963 compared with the production in the previous year reached 49 per cent. The estimated demand of ethylene in 1967 will be approximately 1,031,000 metric tons, equivalent to 34 per cent annual increase.

# TABLE 4 (Unit: 1,000 metric tons)

19 <b>5</b> 8	1959	1960	1957	1962	1963	1954 *
14	44	78	107	232	346	438

+ Annual ethylene capacity as of April 1964.

Table 5 shows annual changes in the utilization pattern of eracked products in weight per cent.

Because it is difficult, as has been pointed out, to attain the balanced utilization of all by-products economically and as the situation is further aggravated by the recession in Japan for the past few years, three petrochemical complexes which were authorized by the Government during 1960 and 1961, have been forced to delay the completion of their plants until 1964.

# 7. RELATIONSHIP BETWEEN ESTIMATED DEMAND AND YIELD PATTERN

According to the estimate prepared by the Industrial Structure Investigation Council of the Japanese Government, the demands of basic intermediates are as shown in table 6.

Ethylene, propylene and butadiene are supplied from petroleum sources; but benzene, toluene and xylenes (BTX) have been and will be supplied from both petroleum and coal. Actually, in 1963, the petrochemical industry supplied 33 per cent of the total benzene requirement of 246,000 metric tons, 72 per cent of 132,300 metric tons toluene and 88 per cent of 71,300 metric tons xylenes. The shares of BTX supplied by petroleum sources are increasing year by year.

Among the by-products of naphtha cracking, which are not yet utilized fully for chemicals, there is iso-

		<b>196</b> 1	/962	1963 (A)	1963 / 1
Off-gas	For chemicals	5.7	4.4	4.1	5.1
		(27.8)	(22.0)	(20.2)	(21.7)
	For fuel.	14.8	15.6	16.2	18.4
		(72.2)	(78.0)	(79.8)	(78.3)
Ethylene	For chemicals.	18.7	19.2	19.4	20.7
		(99.5)	(100.0)	(100.0)	(100.0)
	For fuel.	01	0.0	0.0	0.0
		(0.5)	(0.0)	(0.0)	(0.0)
C <sub>a</sub> fraction	For chemicals .	6.7	6.6	8.1	16.5
-		(42.4)	(40.7)	(50.6)	(100.0)
	For LPG	8.0	7.8	7.2	0.0
		(50.6)	(48.1)	(45.0)	(0.0)
	For fuel.	1.1	1.8	0.7	0.0
		(7.0)	(11.2)	(4.4)	(0.0)
C <sub>4</sub> fraction	For chemicals	7.6	7.7	7.8	8.0
		(63.9)	(66.4)	(70.9)	(80.0)
	For fuel.	4.3	3.9	3.2	2.0
		(36.1)	(33.6)	(29.1)	(20.0)
Crkd. Naph.	For chemicals	8.0	15.7	15.0	14.1
		(39.8)	(70.0)	(70.1)	(82.5)
	For fuel.	12.1	6.8	6.4	3.0
		(60.2)	(30.0)	(29.9)	(17.5)
Rosidue	For chemicals	2.7	1.4	1.9	5.6
		(57.4)	(23.3)	(27.5)	(100.0)
	For fuel.	2.0	4.6	5.0	0.0
		(42.6)	(76.7)	(72.5)	(0.0)
Others	For chemicals	1.7	1.4	1.3	0.0
		(35.4)	(56.0)	(52.0)	(0.0)
	For fuel.	3.1	1.1	1.2	4.9
		(64.6)	(44.0)	(40.0)	(100.0)
l'otal	For chemicals	<b>51</b> .1	56.4	57.6	70.0
	For fuel.	45.5	41.6	39.9	30.0
	Lees	3.4	2.0	2.5	1.7

TABLE 5 (Unit: wt. per cent)

Note. The figures in parentheses are weight percentages for each product. For 1963, (A) is for all plants in Japan and (B) is for NPCC plant only.

TABLE 6 (Unit: 1,000 metric tons)

	1963	1964	1965	1966	1967
Ethylene	341	520	710	869	1,031
Propylama	147	232	382	392	48
Dutadione	66	84	134	158	181
Densene	251	304	389	439	401
Teluene	136	151	177	284	233
Xylenes	84	97	197	122	139

butylens in the C<sub>4</sub> fraction for butyl rubber, anti-oxidant, etc., and there are polymethyl benzense and neghthalens homologs in the cracked naphtha and/or residue that should be considered for utilization. In the case of NPCC, the residue is being sold for the production of farmes black. Among others, potentially valuable products, namely, C<sub>4</sub> fraction including systogeneradiene, isoprene, piperylene and pentenus should be explored for their utilization.

On the other hand, the processes which yield product patterns most compatible with domands should also be reinvestigated. From this viewpoint, two plants, which warrant notice are operating in Japan. One of them is a high severe (HS) cracking furnace of Stone & Webster Engineering Company type and the other is a sand cracker of the Ruhr-Lurgi type.

It is said that the former furnace is to attain the yield pattern shown in table 7.

Such a satisfactory result is obtained by recycling the others stock produced in the cracking process. It is said that the batadiene context in the C<sub>6</sub> fraction is 63 per cent, equivalent to 3.6 per cent of the total maphile charge and the BTX context in erashed maphiles is 23.6 per cent for banavas, 18.3 per cent for tolusme and 10.2 per cent for sylcass and othylbeamses, respectively. The commercial formace of this type is said to have been repeating successfully.

TABLE 7

(Unit: Wt. %)

Linkylune	Proprieta	C. traction	Cracked Napita	Residue	0 <b>5-9</b> 4.
PREF. 1.11.4.1ML -	•• ·· ·· ·				
32.0	9.6	5.8	<b>24</b> . I	7.9	16.8

able. Therefore, the exorbitant import duty imposed on naphtha has been reduced temporarily for limiting petrochemical uses from April of 1964 to meet the anticipated shortage of naphtha in the future.

TABLE 8 (Unit: 1.000 kilo-litre)

Not much is known about the sand cracker in Japan because it has only recently begun its operation. The complex which now operates a sand cracker, however, is considering other processes for its second ethylene project.

The Japanese petrochemical industry has continued the growth rate first experienced six years ago when ethylene production was initiated. The naphtha demand for cracking, including a small amount of catalytic reformate for the extraction of BTX, has sky-rocketed, and the ratio of naphtha for chemical uses to the total oil demand has grown rapidly, as shown in table 5.

As a result, the supply of naphtha to petrochemical complexes in Japan has become less smooth and depend-

Flocal year	Total oil demand	Demand for petrochemicais	Per cent
1957	14,522	35	0.24
1958	16,260	268	1.65
<b>1959</b>	<b>20,8</b> 73	635	3.02
960	29,517	853	2.95
1961 a la la la la la	36,280	1.322	3.64
1962	46,195	2,191	4.74
1963 •	55,434	3,361	6.06
1964 • /	66,666	4,923	7.36
1965 ·	76,826	6,266	8.16
<b>1966 *</b>	88,509	7,472	8.44
967 •	99,774	8,672	1.69
1966 •	112,772	9,780	8.67

· Entimated; the actual figures for 1963 have not yet been released.

# 6. PRODUCTION OF BASIC PETROCHEMICALS FROM HEAVY OILS VIA THE H-OIL PROCESS

# A. R. Johnson and S. W. Ehrlich, Hydrocarbon Research, Inc., United States of America

One of the most significant features of the development of the chemical industry over the twenty years since the Second World War has been the phenomenal acceleration of the use of petroleum-derived raw materials to provide the basic building blocks for the manufacture of a broad spectrum of chemical products. Initially, much of this development centred round areas having large surpluses of indigenous hydrocarbons, particularly natural gas, for which there was no immediate outlet as fuel. The Gulf Coast and south-west regions of the United States are examples of such centres. Under the impetus of the last war, a number of processes were developed on both sides for the synthesis of polymers, detergents, synthetic higher alcohols, etc. These products require as startingpoints basic hydrocarbon chemicals.

Developments in this area in the past ten years have resulted in the creation of a number of petrochemical complexes. These complexes are no longer tied to primary sources of hydrocarbons, but often have a refinery as a nucleus. The complexes have been proliferating at an ever-increasing rate and now constitute a main feature of the industrial landscape in most of the advanced countries of the world.

This conference is addressing itself to the extension of the production of petrochemicals in the developing areas of the world. Since petrochemicals are the basis for so many industries, this is an extremely significant and timely subject for discussion. A considerable part of the consideration will necessarily be directed to those areas endowed with locally available light hydrocarbons derived from crude oil field and natural gas production. The demand pattern for the major petroleum importing areas at present is such that raphtha, and to some extent the other lighter hydrocarbons, are surplus raw materials, which therefore appear attractive for conversion to petrochemicals.

This paper is concerned with the position of the less fortunate countries which must rely on imports for their supply of petroleum and, in turn, rely on petroleum to supply their basic energy requirements. The plight of these resource-deficient areas is not by any means desperate. As the necessary technology for petrochemical manufacture has become more readily available, the key component in a successful petrochemical venture has shifted from possession of resources and technology to access to the market. The experience of many European countries, Australia, India, and Japan demonstrates that the presence of indigenous light hydrocarbon materials is not a prerequisite of the establishment of a petrochemical complex. The chief factor in the final analysis is the converted cost of the raw materials.

In arriving at this converted cost of raw materials, a careful and searching assessment of the available stocks must be made. Over the life of the plant, raw material costs are the largest single cost item - larger by far than even the plant cost. At present, heavy high sulfur crude oils are tending to become surplus owing to the recent moves on the part of local authorities in the many developed industrial areas to restrict the sulfur content of fuel oils. Often these restrictions limit sulfur content to levels which cannot be met with many of the crudes currently comprising a large part of international oil trade. The possibility then arises of obtaining these materials under economically attractive terms. This paper will discuss the technical and economic features of the H-Oil and Hy-C processes which are technically demonstrated, economically attractive techniques for conversion of heavy hydrocarbons to lower boiling materials. A portion of the light materials produced can be diverted as feedstocks for petrochemical facilities. This, then, presents a basis for a petrochemical-refining complex based on the use of heavy oils as raw materials. A petrochemical complex consisting of light hydrocarbons derived from these heavy oils can make an important contribution to both local economics and the balance-ofpayments position of a developing country.

Conversion of residue and heavy oils into lighter, more valuable products requires adjustment of the carbonhydrogen ratio by either decreasing the former or increasing the latter. Coking is the most common and effective method of removing carbon, and visbreaking, de-asphalting and other processes accomplish the same end. The alternative approach, adding hydrogen, has never suffered for lack of interest, but it is only recently that this approach has been reduced to commercial scale practice at a refinery on the United States Gulf Coast.

As early as 1913, however, Bergius in Germany was experimenting with hydrogen-cracking of Galacian and Romanian residua. This German experience culminated in the wartime coal hydrogenation plants, which produced significant quantities of aviation gusoline. Since the commercial practice of residual hydrocracking has been so long aborning, it is of interest to consider briefly some of the technical problems involved. Essentially the process involves cracking oil at elevated temperatures in an environment which will promote hydrogenation of the cracked molecules. This hydrogenation prevents formation of coke, and leads to products of a higher degree of saturation than those produced thermally (i.e., in coking, visbreaking, etc.). In order to maintain this hydrogenating environment, the reaction is conducted at fairly high hydrogen partial pressures in the presence of a suitable catalyst.

In hydrocracking residue and other heavy oils, the fixed bed reactor, usually employed, poses some rather serious problems. First, the over-all reactions are highly exothermic and it is necessary to provide a suitable means of temperature control. In a fixed bed catalytic system this control would usually be achieved by a complex system of inter-bed quenching. Second, the tendency of these feedstocks to deposit carbon, metals and entrained materials can, in many irstances, cause severe pressure drop and/or poor flow distribution in fixed hed systems. Another problem related to the last one is the necessity for removing deactivated catalyst for replacement. While the catalysts used are relatively inexpensive, efficient operation of a fixed bed system would generally require swing reactors.

In the development of the H-Oil and Hy-C processes, a new approach has been taken to the reactor system, in order to eliminate or minimize these difficulties. This work has led to the development of the ebullated bed which is a basic feature in these processes. In this reactor system a liquid phase passes upward through a bed of catalyst at a velocity sufficient to maintain the catalyst particles in continuous random motion. This liquid

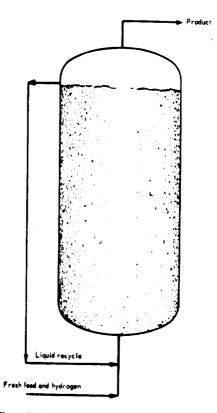


Figure I. H-Oil reactor showing the ebulated bed



Pigure 3. Seale model of H-O4 mit



Figure III. Industrial H-Oil unit

velocity can be achieved in a number of ways, one of which is a liquid recycle as shown in figure I. A hydrogen rich gas phase passes upward through the liquid-solid system providing the requisite hydrogen partial pressure.

This reaction system offers many advantages over convestional fixed bed systems, chief among which are the following:

Isoshormal reaction conditions. The over-all reactions are highly exothermic and, the mixed conditions of this reactor system provide encellent temperature control without elaborate and costly quench systems. Undesirable temperature sensitive reactions are thereby controlled extending useful estalyst life.

Catalyse withdrawal. Catalyst can be added to, or withdrawn from, an obullating bod on either a continuous or an intermittent basis. This feature permits continuous operation at an equilibrium catalyst activity, avoiding the change in product quality with time often encountered with a fined bod of agoing estalyst. Depending on economies and value of catalyst, regeneration may be performed ex-situ in equipment designed for this specific task. Pressure drop. Since the catalyst is in a state of constant, random motion, there is no tendency for pressure drop to build up as a result of accumulation of foreign materials.

A 2,500 DPSD H-Oil unit was installed at a major oil refinery on the United States Guif Coast to confirm, on a large scale, the technical innovations of the process. Figures II and III are photographs of a scale model and of the unit itself. This unit has been operated on atmospheric and vacuum residue, cracked gas oils and various mixtures, and operating results have verified the scale up of the pilot plant results obtained on these feedstacks with respect to reactor design, product yields, suffur removal, etc. The unit has effectively demonstrated the feasibility of the ebullated bed technique on a large scale.

The Kuwait National Petroloum Company recently announced its intention to erect a 95,000 BPSD refenery in Kuwait. This refenery will employ H-Oil and Hy-C as basic processing tools in achieving its goal of maximum distillate yield. Whether calculated on the basis of total hydrogen consumption or on fluctuated processed, this is the largest hydrocracking-hydrogenation complex announced to date.

Figure IV is a flow diagram of a typical H-Oil unit. Residuum or heavy oil is contacted with hydrogen, preheated and sent direct to the reactor. Since the reaction is strongly exothermic, and the reactor system is essentially isothermal, the mixed feed does not require preheating to the reactor temperature. Actually, the sensible heat requirement of the feed provides the means of reactor heat removal. This results in considerable net savings in furnace duty when compared to quenched, fixed bed reactor systems. Oil is circulated from the top of the ebullated bed back to the bottom in order to provide the upward velocity necessary to maintain an ebullated bed.

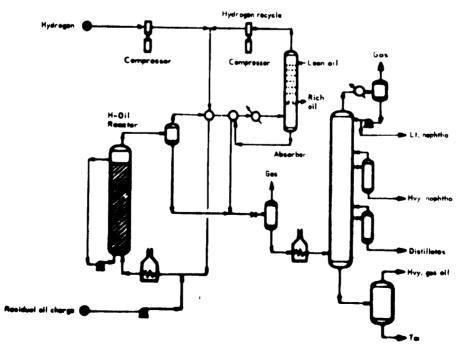
Hot effluent material is separated into liquid and vapour fractions. The vapour portion thereof is exchanged and cooled in order to provide the necessary recycle hydrogen stream. In this particular instance we have shown an absorber operating on this circulating hydrogen stream to remove light hydrocarbons in order to maintain adequate hydrogen purity. If the net input and production of these light hydrocarbons is low, it is feasible to dispense with this step and to purify the circulating gas by means of a purge. In the event that the make-up hydrogen is produced by steam reforming of the purge gas, this purge leads to no net loss of hydrogen, but imposes the requirement of additional compression to return the hydrogen to the system pressure.

Condensed effluent is fractionated into the desired end products. The fractionation system installed will vary with the particular net products required. The case shown in figure IV represents a single-pass operation producing a full array of distillate and residuum products. It is often desirable to recycle the vacuum gas oil to extinction, thereby maximizing the yields of distillate and lighter materials.

To illustrate the yields and product properties obtained by H-Oil processing, the data in table 1 have been prepared. Product yields obtained when processing various fractions of Kuwait crude to various levels of severity are given, together with more significant product properties. Table 2 presents investment and operating requirements for the cases given in table 1. All of the cost data are on a United States Gulf Coast erected basis, and represent battery limits facility only. Fractionating equipment is included but the production of hydrogen is not included.

In order to provide a basis for the estimation of product yields obtainable from the use of H-Oil naphtha as petrochemical feedstock, the data in table 3 have been prepared. This is a detailed inspection of a naphtha fraction obtained from an H-Oil effluent, and for the purpose of comparison, the same data are given for a naphtha derived from Kuwait crude oil. While there are some differences, the similarity between these streams is quite marked. Effectively then, H-Oil effluent materials are equivalent to virgin petroleum fractions as chemical feedstocks.

As an illustration of the utilization of heavy crudes plus H-Oil processing for petrochemical production, let us consider the processing of 35,000 BPSD of a 19°API, 4.3 per cent Sulfur Middle East crude oil. In most of the developing areas of the world the market for petroleum products is heavily oriented toward the distillate products. These materials are also in demand in Europe, and are a valuable commodity for export. On this basis we have assumed in this example that distillates (kerosene, diesel



Plane IV. Turind B-Od for domain

Case Feed	A Vac. restil.	J Vac. par ref	C Aimes. result.	D Asmos. restd.
•API/•,\$	8.0/ <sub>5.4</sub>	21.0/3.2	13.7/ <sub>4.1</sub>	13.7/ <sub>4.1</sub>
Operation	Mild desuif.	Max. dist.	Moderate sever.	Max. diet.
H.S. NH., wt. %	2.6	3.3	3.4	4.0
CC. w. %	1.5	4.4	3.9	5.5
C		1.6	1.9	2.6
C, , vol. % C,-180°F, vol. % }	6.3	6.1	3.9	7.0
180-290 F, vol. %		12.8	5.9	12.2
290-700°F, vol. %		84.8	43.1	80.0
Fuel oil, vol. %	96.2		51.1	<b>S.</b> 0
H <sub>1</sub> consumption, SCF/B	399	1,000	1,070	1,3 <b>90</b>
C-180. • APL		84.0	82.0	82.0
• F-1 cl/3 cc		62/77	60/75	60/75
180-290. API		64.0	62.0	62.0
P/N/A		45/35/20	<sup>50/</sup> 30/20	50/ <sub>30/20</sub>
290-700, •API.		34.0	40.0	32.3
D.I		50	50	4
	14.0		18.0	5.0
<b>* 8</b>	3.0	-	1.7	5.0

# TABLE 1. H-OIL/HY-C PROCEEDING OF KUWAIT PRACTIONS Yield and product data

# TABLE 2. H-OIL/HY-C PROCEEDING OF KUWART PRACTICING Investment and operating requirements

Case *	A		С	₽	
Pool	Pac. restd.	Vac. pas ell	Atmos. reald.	Atmas. restil.	
Operation	Mild doulf.	Max. dist.	Moderate sever.	Maz. dit.	
Capacity	10,600 BPSD	10,000 <b>BPS</b> D	10,000 <b>BPSD</b>	10,000 3PSD	
Est. investment b	\$2,000,000	\$3,300,800	\$3,600,000	54,708,000	
Est. utilities Fuel, MMBTU/hr Power, kW Ceoling water, GPM	25 1,500 1,500	60 3,300 2,000	70 3,700 2,300	80 4,400 3,300	
Est. catalyst cons., c/bbi	6	4	6	12	
Oper. labour, men/shift	2	2	2	2	

· Robra to data in table 1.

· United States Gulf Coast erected basis -- includes fractionation -- battery limits only.

feel, etc.) will be the only feel products produced. tionated to yield light maphths, heavy say not been considered. It would be entirely practical and a heavy ter which is utilized as plast and feasible to make a full line of petroloum fuel products, together with the basic petrochemicals, but this would not add significantly to the illustration.

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m io p in an H-Oil/Hy-C unit which yields aspithas, o and a heavy ter which is utilized as plant fuel. All of gas oil builting between the distillate fractions and ter is respond to extinction.

TABLE 3. COMPARISON OF H-OIL AND VIRGEN NAPHTHAS.

Stock	Naphtha from II-OU processing of California residuum	Kuwait virgin naphtha
18P-200°F		
Component analysis		
iC, wt. per cent.	23.1	16.4
n C <sub>s</sub> wt. per cent	28.7	28.1
iC <sub>s</sub> wt. per cent	23.5	23.3
nC <sub>6</sub> wt per cent	14.1	23.8
Methy Cy Ca wt. per cent	6.2	4.2
Cy Cs wt. per cent	3.3	3.0
Benzene, wt. per cent	0.8	1.2
	100.0	100.0
200 <b>-400 F type analysis</b>		
Parafins, wt. per cent.	45.0	58.5
Naphthenes, wt. per cent.	40.0	25.0
Arometics, wt. per cent	12.0	16.5

naphtha made in the pyrolysis step, are processed in an extraction unit to yield an aromatic extract and a paraffinic rafilmate. The aromatic extract, containing  $C_8$  through  $C_8$  aromatics is sent to a fractionation system, where it is separated into the separate aromatic building blocks — benzene, toluene, and xylenes. In this present instance, the xylenes have not been separated into the various isomers.

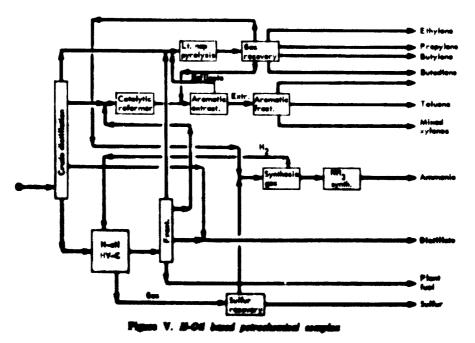
The light naphthas from both crude and H-Oil are mixed with raffinate from the aromatics extraction unit and pyrolyzed to yield a full array of olefins and the aromatic rick naphtha referred to in the discussion of the aromatics extraction unit. All of the light saturated hydrocarbons are recycled to maximize yield of olefins.

Gases collected from all of the processing units constitute the feedstock for synthesis gas manufacture. The H-Oil gases have a significant  $H_9S$  content, which is removed and converted to sulfur. The synthesis gas facility produces hydrogen for the H-Oil unit as well as the raw material for ammonia synthesis. The ammonia made rounds out the list of basic petrochemical building blocks made in this hypothetical plant.

This entire exercise has been predicated on a minimum of restraints or specific product requirements. To match given situations relative production rates of the products can be varied over a considerable range. To cite a few examples: more ammonia and/or synthesis gas derivatives could be made at the expense of olefin production, alternatively, more olefins — less synthesis gas derivatives, and so on.

Very few of the products made in this facility are items of commerce traded over large distances. The only real exceptions being the fuel products and aromatics. Generally, a plant such as this would only be built as part of a larger complex including the downstream processing facilities. A detailed discussion of the downstream processing possible is beyond the scope of this paper, but figure VI has been included to illustrate some of the possibilities.

In any event, production of the building blocks is a convenient breakpoint to consider the economics of the scheme. Downstream processes should stand on their own economic basis when evaluated in terms of a fair feed price. For that matter the downstream processing may very well be in the hands of another organization having the specific technical fabricating and marketing skills required for successful operation in certain of the newer fields such as plantics or fibres. Table 4 presents a



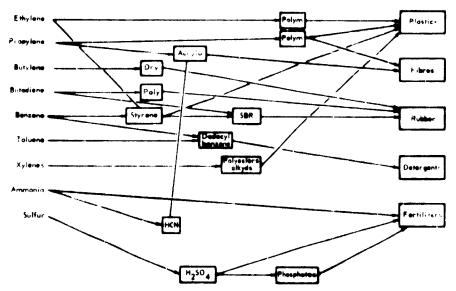


Figure VI. Possible unification of basic petrochemical building blocks

summary of the production of the basic petrochemicals and fuel products achieved when processing 35,000 BPSD of a heavy, high sulfur crude oil. Values have been assigned to the products based on current published European and United States prices. These are necessarily arbitrary and must be modified to reflect the realities of any specific situation.

Table 5 summarizes the costs involved in this complex. Plant investment includes the processing facilities described above, and shown in figure V, as well as the necessary officies, utility generation facilities, and the like. The plant has been valculated to be on a self-sustaining basis with

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respect to fuel and power. Waste gases and H-Oil tar provide all of the fuel requirements, both for process heat requirements and for power and steam generation. With this basis then the direct operating costs consist only of the labour, estabyet and chemicals and operating and maintenance materials and supplies.

Table 6, which summarizes the over-all plant economies, underscores the attractiveness of this scheme. While the capital requirements appear high when compared with \$300-600 per barrel of daily capacity usually considered for a simple refinery, the investment is handsomely returned by virtues of the more valuable products achieved.

#### TABLE 4. H-OIL PEPERCHINGCAL COMPLEX

Over-all plant material balance and great margin

<b>h</b> an	(Castilly)	that price	<b>b</b> yr.
ipur - 19°A25, 43 per cont 8 Middle Bast crude Nadace	35,000 <b>3170</b> D	\$1.49/D	23, 100,00
Negricas Pregrias Detributo Detributo Negricas N	110 Min. 7/80 73 Min. 7/80 37 Min. 7/80 39 Min. 7/80 30 Min. 7/80 120 Min. 7/80 130 Min. 7/80 380 Min. 7/80 380 Min. 7/80 38 Min. 7/80	5 100/16.T. 5 100/16.T. 5 00/16.T. 5 00/16.T. 5 00/16.T. 5 00/16.T. 5 00/16.T. 5 00/16.T. 5 00/16.T. 5 00/16.T. 5 00/16.T. 3 4.00/10	3,000,00 2,779,00 1,799,00 2,129,00 2,129,00 3,109,00 1,209,00 1,209,00 1,209,00
Totas.			56,409,69 59,369,69

# TABLE 5. N-OIL PETROCHEMICAL COMPLEX Capital and operating requirements

Sec. 1

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# TABLE 6. H-OIL PETROCHEMICAL COMPLEX

Economic summary

United States dollars

57,000,000

29,360,000/yr.

7,400,000/yr.

21,960,000/yr

Years 2.6

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	United Seates dollars	
Capital requirements Plant Republics Working capital	50,000,000 2,000,000 5,000,000	Total capital requirement Gross operating margin Direct operating costs Gross profit
TOTAL	57,000,000	Years to pay out capital
Direct operating costs Labour — 350 men at \$4,000/yr./men Catalysis and chemisals. Meterials and suggiles Incurance.	3/)**. 1,400,000 1,000,000 1,000,000 500,000	In summary then, it is our opinion t nove hydrocarbons need not preclud of an economically attractive petro
TOTAL MARCT CASHE	3,900,000	and forther, heavy high sulfur crud through H-Oil can often be an a

that lack of indigede the establishment ochemical industry, des when processed attractive feedstock choice in such a plant.

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# 7. MODERN METHODS FOR THE PRODUCTION OF AROMATICS, OLEFINS AND PARAFFINS

# K. H. Elsenløhr, Lurgi Gesellschaft für Mineralölktechnik m.b.H., Federal Republic of Germany

## INTRODUCTION

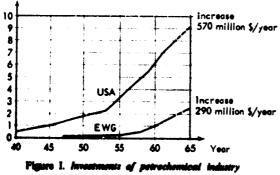
In the last two decades the organic chemical industry has undergone major changes in its development. Coal has been replaced by natural gas and petroleum, and natural products have been ousted by plastics and synthetic fibres. Owing to super tankers and pipe-lines, the location of great and old branches of industry has nearly dwindled into insignificance, piston engines have been superseded by jet engines, and every day, owing to thousands of innovations, new tasks arise which, in fact, are not realized by the public. It must always be borne in mind that the values of our plants and industries, which go to the billions, are endangered by technical progress. A process which is developed today may be replaced by a more economical one tomorrow.

This development is best characterized by the sums invested by the petrochemical industry. The steep growth of these investments since 1953 can be gathered from figure 1. In 1962 about \$US 570 million were invested in the United States, whereas in the same period of time \$US 290 million were placed in the area of the European Economic Community to develop the petrochemical industry (1). For the years to come, investments still higher than the sums mentioned are to be expected.

The capacity of the petrochemical industry was expanded mainly in order to produce more aromatics and olefins as the raw materials for plastics, synthetic resins, synthetic rubber, fully synthetic fibres, insecticides, plant protectives, pharmaceuticals and colouring matter.

Further, the petrochemical industry was confronted with the problem how to meet the demand for straight chain paraffins for the production of biologically quick degradable detergents.





**AROMATICS** 

The demand for aromatics of the organic chemical industry was covered over several decades by the production potential of the coal-coking industry, since the coke production furnished a sufficient quantity of aromatics. As the rate of coke necessary to produce one ton of raw steel was decreased by about 50 per cent and the demand for aromatics was increasing constantly, the market could no longer be satisfied by the coal-coking industry. Thus, the conversion products of petroleum became an additional source for the production of aromatics.

Since 1949 the production of aromatics in the United States has been growing constantly and nowadays exceeds the output from coke ovens considerably. For instance in 1962 the production rate of petroleumderived benzene was three times the quantity recovered from coal coking (2), that of toluene eleven times, and that of xylene forty-six times. It should be noted that the figures for toluene and xylene also include those quantities used to blend motor fuels (see figure II).

Sufficient quantities of pyrolysis gasolines from the production of olefins and reformates are now available for the recovery of aromatics. In view of the raw material sources existing in the United States, it is supposed that the production of benzene could still be increased sixfold, that of toluene twelvefold and that of xylenes at least twentyfold.

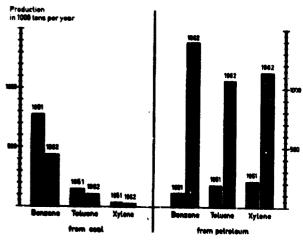


Figure II. Aromatics production in the United States

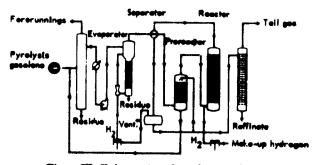
TABLE 1. TYPICAL CONFORTION OF PYRIOLYBB GAROLINGS FROM OLEPIN PRODUCTION

Rew material	Porroloum or Autillatos					
Denzeno a constante a constante a	Wt. %	23	17			
Toluses	Wt. %	12	t6			
Xylence •	W1. %	9	•			
Higher arcmatics	Wt. %	1	3			
Non-aromatics		48	55			
Bromine No		65	56			
Sulphur		0.07	0.0			
Nitrogan		0.0001				
Ожудия	-	0.0005				

· Including ethylbonsons and styrene.

It is not possible to separate benzene, toluene and xylene from pyrolysis gasolenes in one single step (see table 1). A combination of several processes is required.

By hydrorefining, e.g. to the Farbwerke Hoechst AG Process (3) or the process of Farbenfabriken Bayer AG (4), the pyrolysis gasolone is treated under pressure with hydrogen-bearing gases in the presence of a catalyst (see figure III). The unsaturated hydrocarbons and the sulphur, oxygen and nitrogen compounds are hydrogenated, while the aromatics are not affected. It is noteworthy that these processes reduce sulphus to 1 mg. thiophene per kilo and less.



Pignee III. Hydrogenation of pyrolysis gausiens — Process of Farbworks Höchst A.G.

For economic reasons, hydrogenation is concentrated on benzene-toluene or benzene-toluene-xylene cuts. The forerunnings and higher boiling components are separated by distillation prior to hydrogenation. This increases the concentration of aromatics, reduces the hydrogen consumption, improves the raffinate purity, and cuts down the plant investment costs.

Thus, by separating a benzene-toluene cut (BT cut), the rate of feed to be hydrogenated is reduced by 51 weight per cent (see table 2). The consumption of hydrogen decreases by about 80 volume per cent, proportionally with the feed rate and bromine number. When separating a benzene-toluene-xylene cut (BTX cut), the size of the hydrogenation plant can be reduced by 30 per cent, and only 30 per cent of the hydrogen, required to hydrogenate the entire pyrolysis gasolene, is consumed (see table 3).

The forerunnings and residues from pyrolysis gasolene distillation can be processed to high octane motor gasolenes by a mild selective hydrogenation with little consumption of hydrogen by the process of The British Petroleum Co. Ltd. (5), (6), or the process of Farbenfabriken Bayer AG (4).

Moreover, the catalytic reforming of petroleum distillates of the gasolene boiling range in the presence of a platinum catalyst furnishes aromatics by dehydrogenation of naphthenes (see figure IV). The liberated hydrogen is often used for refining the crude material in a preliminary stage (7). Here again, benzene, toluene and xylene may be concentrated by preliminary distillation (see table 4).

More recently the raw material source, particularly for the production of benzene, has been broadened still further by dealkylation processes (8), (9), so that a more than ample supply of petrochemical aromatics is now available.

On a technical scale, aromatics are almost exclusively separated from non-aromatics of the same boiling range by liquid-liquid extraction (hereinafter referred to as extraction). A prerequisite for the application of the process is that the organic solvents used and the mixture to be separated form two phases. The solvents and aromatics are separated by distillation. As solvents only such materials are of use which contain a polar group.

TABLE 2. FRACTIONAL DISTRILATION OF A PYROLYHE GANOLINE TO RECOVER A BT CUT

	Pyrotyste sasoione	Pere- runnings	BT distillate	Residu
Yield	6 100	24	49	27
Content of :				
Bennen		1.3	32.0	_
Tolueno	/ 16.6		33.0	1.5
B + T	32.6	1.3	65.0	1.5
Bennene Ices	<b>~</b> -	2		-
Tolsee logs	<b>~</b> -	_	<b></b> '	2.5
Bromine No. (g/100 ml.)	73		27	_

	 	<b>_</b>		Prevalgeda Onuclear	Para- runnings	BTX distillare	Residur
Yield	-		<b>W</b> t. %	100	20	70	10
Content of:							
Donasno			- WL %	18.8	2.0	26.4	
Tohane			- WL %	16.8		24.2	
Xylenes •.	 	•	W1. %	8.7	-	11.9	3.8
<b>B</b> + <b>T</b> + <b>X</b>	 		<b>W1.</b> %	44.3	2.0	62.5	3.8
Noncone loss	 		WI. %		2.1	907 s	
Xylone loss	 		W1. %			_	4.6
Bromine No. (g/100 ml.)	 	,				33	

TABLE 3. FRACTEDNAL DEPTELLATION OF A PYROLYSE GAROLENE TO RECOVER A BTX CUT

\* Including othylbonzone and styrene.

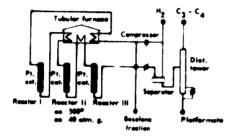


Figure IV. Production of aromatics by reforming platforming process

The polarity shall, as for instance in the case of water, not be too high because solubility for aromatics decreases with increasing polarity. On the other hand, solubility should not be too low, since the solubility for nonaromatics increases to a greater extent than that for aromatics with decreasing polarity. For economic reasons solvents with a boiling point, which exceeds that of the aromatics to be extracted, are given preference.

Figure V illustrates the process flow of liquid-liquid extraction using a high-boiling solvent.

The solvent is fed to the top of a multi-stage extractor where it travels downwards and preferentially dissolves the aromatics. The mixture to be reparated is charged to the centre of the extraction tower. The solvent loaded with aromatics leaves the tower bottom while the nonaromatics go overhead. The extract is distilled off from the extract phase and subsequently fractionated into pure products. As aromatics and non-aromatics shall be separated completely, a reflux has to be recycled to the extraction tower, similar to other separation processes using the countercurrent principle. Part of the aromatics is therefore returned to the base of the extraction tower.

The above described principle underlies the Udex Process developed jointly by Dow Chemical Corporation and Universal Oil Products Company (10), (11), (12). The process has been applied in about forty plants to a variety of feedstocks of different origin, including hydrogenated coke oven light oil. The process uses disthylene glycol (boiling point 250°C.) or mixtures with triethylene glycol (boiling point 286°C.) as solvent.

The extraction process is operated at temperatures above 100°C. The Udex Process includes, apart from the extraction equipment, facilities for the continuous

			Reformate	BTX-cul
Yield		W1. %	100	64
Content of:				
Benzene		Wt. %	3.5	5.1
Toluene		Wt. %	19.0	30.0
Xylenes *	• • •	Wt. %	21.5	32.2
$\mathbf{B} + \mathbf{T} + \mathbf{X}$	•••	Wt. %	44.0	67.3
Non-aromatics		Wt. %	<b>40</b> .0	32.7
Higher aromatics	• •	Wt. %	16.0	

TABLE 4. COMPOSITION OF A HEAVY GASOLENE REPORMATE

· Including ethylbenmene.

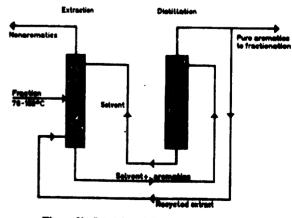


Figure V. Principle of liquid-liquid extraction

regeneration of the solvent and for the solvent recovery from rafilmate and extract by water washing. Last traces of olefins are removed from the extract by clay treatment at increased temperatures. The process furnishes high yields, and the aromatics recovered are of optimum purity.

Sulpholane with a boiling point of 286°C. is used commercially as solvent for extraction by Shell Development Company (13), (14), (15).

Shell has successfully extracted aromatics with sulfolane at its Rho Oil Refinery in Italy. A catalytic reformate fraction containing 68 per cent non-aromatics is processed to yield a 99.8 per cent aromatic mixture in a total yield of about 96 weight per cent, the losses consisting only of tohuone and xylenes. The benzene yield amounts to approximately 99.8 per cent. The following purities were obtained (see table 5):

At Shell's Stanlow Refinery in the United Kingdom a Universal Oil Products Co. Udex unit has been revamped for sulpholane operation. Normally there are extracted high octane blending stocks from reformate but the unit also can produce an aromatics yield in the range of 99 per cent purity.

Sulpholane process is a combination of liquid-liquid extraction with extractive distillation as shown in figure VI. The feed contacts lean solvent in an extractor. The resulting solvent phase enters an extractive distillation tower which yields aromatic-rich solvent as a bottoms and an overhead backwash stream that returns to the extractor. The raffinate from this arrangement leaves the top of the extractor.

One advantage claimed for this arrangement is its ability to reject both light and heavy non-aromatics from the extract. The non-aromatics leaving the extractor in the solvent phase are predominantly light, and can easily be stripped out overhead during subsequent extractive distillation. The heavy non-aromatics are rejected directly from the extractor in the rafinate phase. The flow diagram given in figure VII shows Shell's process sequence for extracting mixed benses, toluene and xylenes from a catalytic reformate fraction containing about 50 per cent aromatics.

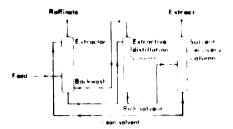


Figure VI. Combination of extraction with extractive distillation

Fresh feed enters an extraction tower, e.g. a rotating diac contactor that operates at increased temperature (about 50 to 100°C), representing a compromise between solvent selectivity and hydrocarbon solubility. The extent of aromatics recovery depends jointly on the solventto-feed ratio and the number of extraction stages, e.g. ten to fourieen stages.

Effuent from the extractor bottom enters near the top of the extractive distillation tower. Bottoms product from this tower is the extract stream containing solvent and aromatics, which then goes to conventional distillation for recovery of the mixed aromatics as overhead product. The sulpholane is steam stripped in the lower section of the latter vessel before leaving as bottoms. This removes last traces of hydrocarbons.

The solvent content of the mixed aromatics product is very low because of the fractionation the aromatics undergo. On the other hand, losses of sulpholane with the non-aromatics are minimized by water-washing the raffinate. The water necessary for this step can be conveniently taken as that which leaves the recovery tower with the aromatics; after washing the raffinate, this spent water is then reused as stripping medium at the bottom of the recovery tower.

The consumption figures of the Sulpholane Extraction Unit at Rho Refinery are shown in table 6.

N-methylpyrrolidone with a boiling point of 206°C. is used by Lurgi Gesellschaft für Mineralöltechnik mbH

	Densene	Tokune	Zylone
Spec. gravity 15/4°C	0.8842	0.872	0.8694
ASTM analysis:			
<b>IBP •C</b>	79.3	110.1	138.3
5 per cent	79.8	110.3	139.0
95 per cent	80.1	110.5	140.1
FBP °C	80.2	110.5	140.3
Non-aromatics	0.06	0.01	0.01
Benzene	<b>99.</b> 93		
Toluene	0.01	99.99	0.02
Xylenes + ethylbenzene		_	99.97
Freezing point °C	5.39	_	

TABLE 5. SULPHOLANE PROCESS, PURITY OF AROMATICS

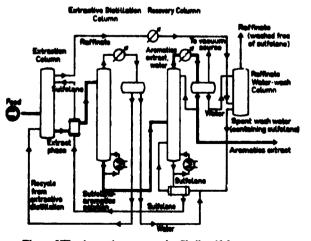


Figure VII. Aromatics recovery by Shell sufficience process

TABLE 6. CONSUMPTION PIGURES OF THE SULPHOLANE PROCESS

	Units per tan Teodatack	Units per ton of recovered aromatics
Utilities. •		
Steem (I)	0.87	2.15
Cooling water (cu.m.)	16	96
Electric power (kWh)	6	16
Solvent b (kg.)	0.2	0.54 = 3.60 DM/t
Composition of feedstock		
Non-aromatics (vol. per cent)	68 6	
Benzene (vol. per cent)	5.2 \	
Toluone (vol. per cent)	16.1	
Xylone + ethylbonzone (vol.		~ 37 Wt. per cent
per cent)	10.1 J	
Yield :		
Bonsone + toluene + xylenes	+ athvi-	
benzene		96 wt. mer cent

\* Distillation inclusive

\* Price of Sulpholane: 6.70 DM/kg.

on a technical scale as selective solvent in the so-called Arosolvan Process (16).

The solvent is manufactured in commercial scale plants and used for instance to concentrate acetylene, produce butadiene and purify natural gas. It is entirely neutrel, thermally stable and distillable at atmospheric pressure without destruction. Thus, all parts of the plant are made of normal steel.

The high solvent capacity of N-methylpyrrolidone (NMP) can be easily adjusted over a wide range of strength by addition of water. Owing to its physical properties, e.g. its low melting point of  $-24^{\circ}$ C. and its low viscosity, extraction can be carried out at low temperatures, contrary to other processes.

The solubility of NMP in non-aromatics is a function of the water content. In case of non-aromatic mixtures recovered as rafinate phase from the extraction of hydrogenated pyrolysis gasolines and reformates, the solubility for a water content of 10 to 20 per cent is between 3 and 0.5 volume per cent. Owing to its extremely high partition coefficient, only small quantities of water are required for NMP recovery. The water used for this purpose returns to the process so that the water cycle is entirely closed.

In lieu of an antisolvent or aromatics reflux, the Arosolvan Process uses a "mixed reflux", consisting of aromatics and non-aromatics. The non-aromatics contained in the "mixed reflux" are low boiling hydrocarbons. They are present in all hydrorefined products and reformates. Because of this "mixed reflux", the higher boiling non-aromatics, physically dissolved in the extract in the lower section of the extractor, are replaced by low boiling non-aromatics which are easy to separate from the aromatics by distillation. This applies in like manner to paraffins, isoparaffins, naphthenes and olefins in particular. Hence, an additional clay treatment at increased temperature and pressure to remove olefins is not required. As shown in figure VIII, the solvent is charged to the top of a multi-stage extractor, from which it travels downwards. The mixture to be separated is fed to the centre of the extractor. The non-aromatics insoluble in the solvent pass upwards and leave the extractor at the top, while the solvent flows downwards and becomes loaded with aromatics. In a distillation tower, extract and solvent are separated, the latter being returned to the process. The water, which is azeotropically carried over with the hydrocarbons, is separated and recycled to the extractor together with aromatics-free NMP.

The distillate from extract distillation, aromatics and low boiling non-aromatics, goes to the aromatics stripper where low boiling non-aromatics and part of the benzene are distilled off. The residue, the pure aromatics, is fractionated subsequently. Fractionation towers with a few trays are sufficient for this step.

The non-aromatic hydrocarbons from the top of the extractor enter the non-aromatics stripper where they are separated from the low boiling components, which are supplied, together with the distillate from the aromatics stripper, as "mixed reflux" to the extractor bottom.

Two commercial scale plants using the process described above are now in operation. The first one for the production of benzene, toluene and xylenes from a hydrogenated coke oven benzene/oil gasification gasolene mixture (30 to 90 per cent aromatics) was commissioned in December 1962 at Tokyo Gas, Yokohama Works. The output of the plant, originally sized for a production of 50,000 t. aromatics per year, was increased by small alterations to 65,000 t. aromatics per year.

The yield is as under:

Denzene										99,9	per	cent
Tohene	•	•								<b>99</b> .7	per	cent
Xylenes	+		lhy	/ib	ŧ.	ne				96.8	per	cent

Calculated over twenty-two months, the average melting point of pure benzene is above 5.50°C., the solvent consumption being 0.02 kg. per ton aromatics. A

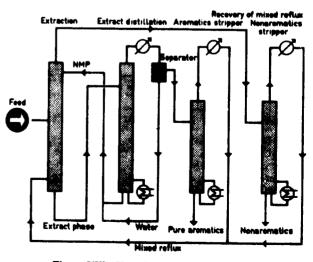
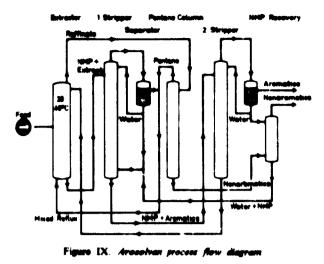


Figure VIII. Flow diagram of NMP process



regeneration of the solvent, for instance by distillation, is not necessary.

In December 1963, the second plant for the production of benzene and toluene from a hydrogenated pyrolysis gasoline with a capac ty of 80,000 t. aromatics per year was commissioned at Erdölchemie GmbH Dormagen, Federal Republic of Germany. Figure IX illustrates the process flow of this plant.

The hydrogenated mixture of aromatics and nonaromatics is supplied to a mixer-settler type extraction tower comprising some 20 to 30 extraction stages. The solvent, an NMP/water mixture, is charged to the top of the tower, from which it travels downwards. The loaded solvent is stripped in two stages. In the first stripper all low boiling hydrocarbons and part of the benzene are distilled off. To avoid pentane losses, this stripper operates under slightly increased pressure. The distilled water is partly returned to the top of the tower. the remainder being supplied to the bottom to maintain concentration. The bottoms product, which is free from non-aromatics, is separated in the second stripper into a distillate, the pure aromatics, and a bottoms product, the aromatics-free solvent. The solvent returns to the extractor.

The rafinate is withdrawn from the top of the extractor and all low boiling hydrocarbons are distilled off in the pentane tower. This tower operates under pressure, too. The distillate of the pentane tower and that of the first stripper are supplied as mixed reflux to the extractor.

The bottoms product of the pentane tower is separated in a washer from NMP by means of the watery distillate of the second stripper. The NMP/water mixture is routed to the bottom of the second stripper. Thus, the water cycle is entirely closed.

However, the process is not at all limited to the production of benzene, toluene and xylenes plus ethylbenzene. It is also possible by means of small alterations to extend the process to the production of  $C_0$  aromatics.

It must be pointed out again that all previous data refer to the extraction of aromatics from non-aromatics and to the distillation of aromatics to produce pure TABLE 7 OPERATION REPUT OF AROBOLVAN PROCESS

			Fok vo	241	EC Dormagen
Feedntock					
Benzone (will per cen	0		56.	5	35
Toluene (wt. per cen			15	R	25
Xylenes + ethylben:	wene (wt pe	r cent)	8.	1	
Non-aromatics (wt.	per cent )		19	6	40
Yield.					
Benzene (wt. per cen	t).		99.9	9	99.8
Toluene (wt. per cen			99	7	99.0
Xylones + ethylbon:	ene (wt. p	er cent)	96.	8	
Purity	,	7	r		r
Melting point <sup>o</sup> C	5 50			5.50	
Spec. gravity	0.884	0.871	0.870	0.884	0.872
Bansone (wt. %)	99.99	Max		99.99	Max.
		0.1			0.01
Toluene (wt. %)	Nax.	99,9	Max.	Max.	<b>99,99</b>
	0.01		0.1	0.01	
Xylenes (wt. %)		Max	99. <b>8</b>		Max.
N		0.1			0.01
Non-aromatics					
(wt. per cent).	Max	Max.	Max.	Max.	Max.
	0.01	0.01	0.1	0.01	0.01
Utility consumption pr	r ton Aron	natics : •			
Stes m * (t.)			1.8	1	1.65
Cooling water . (cu.	.m.).		60		<b>50</b>
Elec: ric power(kWh	)		. 19		25
NMP (kg.)				)2	0.05
NMP Price per kg (I			. 4.		3. <b>50</b>
NMP Loss per ton o	f Aromatic	s (DM)	0.0	16	0.17

\* Including distillation.

• Or an equivalent quantity of heat in form of fuel oil or gas.

• If using air fin coolers water rate can be decreased, electric power consumption being increased.

benzene, pure toluene and a xylene fraction containing m-, p-, o-xylene and ethylbenzene. The separation of xylene isomers will be dealt with later on.

Apart from the consumption of energy and chemicals there are other factors influencing the applicability of a process, such as low investment costs, possibility of home manufacture, adaptability of the process to local conditions, use of other energy instead of steam, air fin coolers instead of water, adaptability of the process to changing raw material composition, easy maintenance as well as easy manipulability. The Arosolvan Process is able to meet all these requirements.

In addition to the almost constant consumption of utilities such as heat, refrigeration, electric power and solvents, the costs are influenced by the size of plant.

Figure X is a graph showing the operating costs per ton of aromatics including fractionation. The mixture to be extracted is understood to contain about 50 to 60 per cent aromatics of the following composition:

Benzene	between 40 and 20 per cent
Toluene	about 40 per cent
	between 20 and 40 per cent

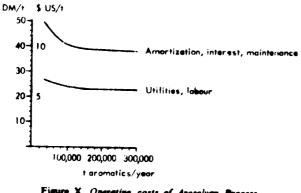


Figure X. Operating costs of Arosolvan Process (costs include fractionation)

For amortization, interest and maintenance 10.5 and 3 per cent. respectively of the investment are set in, the investment bring a turn-key job on the basis of German prices. For operating purposes, 2 men per shift are necessary. The cost price for utilities is as follows:

Steam, 16 alm.g.				12 DM/t.
Cooling water			,	3.50 Dpfg/cu.m.
Electric power.				4 Dofe/kw-hr.
NMP				4 DM/kg.

As already mentioned before, fuel gas or fuel oil may be used instead of steam, which will considerably reduce the utility costs, since about 90 per cent of the energy cost falls to steam. Benzene and toluene are easy to separate because of their boiling points, this is not true, however, of  $C_8$  aromatics as can be seen from table 8. A typical fraction of  $C_8$  aromatics contains e.g.:

ethylbenzene	•					5 to 30 per cent
m-xylene						35 10 65 per cent
p-xylene						10 to 30 per cent
o-xylene	•	•				10 10 30 per cent (17)

All four isomers are recovered commercially nowadays. Ethylbenzene with the lowest boiling point, only 2° below p-xylene, is separated by superfractionation. The production of pure ethylbenzene requires towers with up to 360 trays, a reflux ratio of 1:120 and a heat consumption of about 20 t. steam/t. ethylbenzene. The expense involved is reasonable only in special circumstances.

TABLE 8. CONSTANTS OF ABSOLUTELY PURE AROMATICS

	Crysialliza- tion point (*C)	Bolling point (*C)	Refructive index n <sub>D</sub> 20	Spec. granky al 20°C
Benzene	+ 5.53	80.10	1.5011	0.8790
Toluene.	94.99	1 10.63	1.4969	0.8669
Ethylbenzene	94.98	136.19	1.4959	0.8670
m-Xylene	47.87	139.10	1.4972	0.8642
p-Xylene	+ 13.26	138.35	1.4958	0.8610
D-Xylene	- 25 18	144.41	1.5054	6.8802

Separation of m- and p-xylene by distillation is not possible at all. They are distilled off together from o-xylene. For separation of both isomers from o-xylene, towers with about 120 trays and a reflux ratio of 1:20 are required. The purity of o-xylene is at least 95 per cent, the remainder consisting of both isomers and traces of non-aromatics.

Owing to their different points of crystallization (-48 and +13°C). m- and p-xylene are separated by fractional crystalization. For this purpose the mixture of isomers is cooled down by evaporation of carbon dioxide - Process of California Research (see figure XI) - or ethylene - Lurgi Process (18) - to minus 60 and minus 70°C., and the crystals obtained are removed by means of centrifuges. However, the yield of p-xylene is limited by its eutectic with m-xylene, which consists of 12 per cent m-xylene and 88 per cent p-xylene. Thence, the separated eutectic is partially melted, and the crystal suspension is given to the centrifuge of the next stage, where the crystals are extracted again. This procedure is repeated several times, the temperature being increased from stage to stage. From the last stage p-xylene is withdrawn in liquid condition with a purity of 95 to 99.5 per cent. The mother liquors from the individual stages are returned to the preceding stage. Depending upon the concentration conditions of the initial mixture, the yield of p-xylene amounts to from 50 to 60 per cent only.

The yield of p-xylene can be increased if the mother liquor, which contains about 7 to 9 per cent p-xylene, is subjected to a catalytic isomerization by the process of The Atlantic Refinery Company (19), the Shell Development Co (20), or the Maruzen Oil Co., Osaka, at temperatures of 400 to 500°C., in the presence of hydrogen and under pressure. Owing to isomerization, the p-xylene concentration increases to 19 per cent, the equilibrium concentration. The isomeric product now returns to crystallization. Because of the by-products obtained, which have to be removed from the cycle, the yield cannot be raised at will. A maximum of about 80 per cent can be reached (see figure XII).

The bottoms product of the o-xylene tower contains polymethylbenzenes, particularly in the case of the processing of reformates and cuts with FBP's above

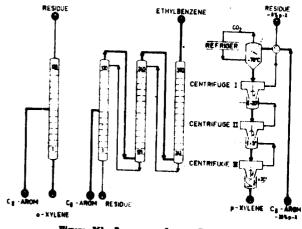
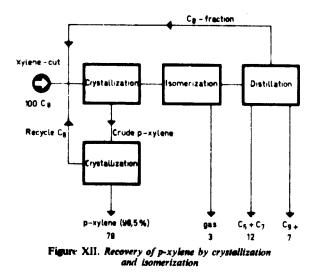


Figure XI. Recovery of pure Centromatics



150°C. By superfractionation, o-ethyl-toluene (boiling point 166°C.) can be separated from 1,2,4-trimethylbenzene, the pseudo cumene (150 trays, reflux 1:13, boiling point 170°C.); and pseudocumene can be separated from hemellitene, the 1,2,3-trimethylbenzene (100 trays, reflux 1:9, boiling point 176°C.). Mesitylene, the 1,3,5-trimethylbenzene, can be separated from the residue only with difficulty. Thus, its manufacture is preferably carried out by isomerization of pseudocumene or its synthesis from acetone.

Durene, the symmetrical 1,2,4,5-tetramethylbenzene, can be enriched by distillation and separated by subsequent crystallization from its isomers because of its high crystallization point of 80°C. The durene yield can be increased by isomerization of the mother liquor, which contains isodurene (1,2,3,5-TMB) and prehnitene (1,2,3, 4-TMB). The technique is similar to the recovery of p-xylene by means of crystallization and isomerization. On the other hand, there is the synthesis, the alkylation of p-xylene with propylene, which leads to 1,4-dimethyl-2,5-isopropylbenzene, which is then treated instead of durene. It is obvious that the recovery of C<sub>8</sub> and C<sub>16</sub> aromatics is profitable only if high rates of reformates are processed.

Summarizing, mention should be made of the use of aromatics. Benzene — the price of which is greatly influenced by offer and demand — is used in the United States mainly to produce styrene and phenol (see table 9) (21). The main consumers can be gathered from the summary: styrene (polystyrenes and synthetic rubber) and phenol (resins, softeners, insecticides, herbicides, detergents). The consumption figure then decreases rapidly. The nylon products only go to 9 per cent, whercas 43 per cent is used for the production of styrene and 19 per cent for phenol.

It must be pointed out that it is not easy to bring production and consumption into line on the basis of statistics. There are disproportions inasmuch as additional quantities of benzene are produced by dealkylation of toluene and  $C_0$  aromatics, which do not appear as production but as consumption. Toluene is directly used to a great extent as a solvent. The dealkylation to benzene has already been mentioned. Other applications are diisocyanate, vinylloluene, benzoic acid and their further decomposition to phenol or caprolactam, toluene sulphonates, the production of dulcifying material, nitrided and halogen derivates. Furthermore, considerable quantities of toluene are used for processing aviation grade gasolene.

The xylene fraction, originally used for the upgrading of motor and aviation fuels and as solvent, becomes more and more the basis for chemical intermediates.

Ortho-xylene, the price of which amounted to DM 270. —/t. in 1963, is the great competitor of naphthalene in the production of phthalic anhydride. Phihalic anhydride is not only an intermediate product for the manufacture of softeners but constantly gains in importance for the isomerization to terephthalic acid by the process of BASF-Henkel. Particularly in Japan, this process has been intensely developed lately, resulting in a simplification and cost reduction of polyester production by avoiding the DMT stage.

Para-xylene, the current price of which is about DM 700.—/t., is almost exclusively employed in the production of DMT and terephthalic acid. Its competitor is toluene, which is applied to obtain 1-methyl-4-iso-propylbenzene by alkylation with propylene, the 1-methyl-4-isopropylbenzene also resulting in terephthalic acid by oxidation.

Of all C<sub>2</sub> isomers, m-xylene is used the least, and most of the production returns to gasolene blends. Another portion is used as solvent or to obtain p- and o-xylene by isomerization. It is of interest to study the way of oxidation to isophthalic acid and its use as comonomer for the production of polyester fibres.

Finally, mention shoul' be made of ethylbenzene, the monomer for the production of polystyrene and the comonomer for SBA rubber. The demand for the production of styrene is almost exclusively met by synthesis, starting from benzene and ethylene. On the other hand it is expected that the production from reformates will gain in significance.

TABLE 9. UTILIZATION OF BENZENE IN THE UNITED STATES OF AMERICA IN 1962

				<u> </u>									-							Per cen
Styrence																				43
Phenoi																				19
Nylon 66 and 6																				9
Synthetic deterg																				6
Maleic anhydrid																				4
DDT																				3
Chlorobenzene																				2
Aniline																				2
Benasne hexachi	loi	rid	le i	ĥ			•													-
Nitrobenzene .					•	·	•	·	•	·	·	·	·	•	•	•	•	·	·	1
Exports																				7
Miscellaneous.																				- Å

Of the  $C_0$  isomers, pseudocumene, the 1,2,4-TMB, is of commercial importance for the production of trimellitic anhydride (TMA), which is the source for alkyl resins, plasticizers for vinyl resins and non-flat-spotting nylon tyre cord.

The difficulties involved in the recovery of mesitylene have already been mentioned. The oxidation product, trimesic acid, becomes more and more important to the production of alkyd resins, plasticizers and moulding resins.

Of the  $C_{10}$  aromatics, durene — the 1,2,4,5-TMB — is of particular significance. It is used to produce pyromellitic acid — a benzene-tetracarboxylic acid — in form of its dianhydride by a gas phase oxidation process similar to o-xylene oxidation. Pyromellitic anhydride is the raw material for the production of high temperature resistant synthetic resins of the polyimide type. Thus the synthetic materials come into the possession of a field which up to now was reserved for metals only because of their high temperature resistant property.

#### OLEFINS

Compared to current demands, the amount of ethylene and propylene obtained as by-products from the low temperature separation of coke oven gases is a triffe. Furthermore, this method of production is becoming obsolete.

With the introduction of the thermal and catalytic cracking processes for the conversion of high boiling hydrocarbons to upgraded motor gasolene, the basis has been considerably extended. In addition, there are now modern processes, specifically developed for the production of olefins on a broad raw material basis. It is possible nowadays to generate olefins from all hydrocarbons and their mixtures, from ethane up to crude oil.

Expressed as a percentage, the production of ethylene in the United States of America is as follows: 50 per cent from cracking of natural gas, e.g. ethane and propane, 38 per cent recovered from refinery gases, and 12 per cent by cracking of petroleum distillates. In Europe, however, the dominant portion is generated from naphtha.

As can be gathered from figure XIII, the production of ethylene has developed rapidly since 1953. The curve does not show any saturation value. On the other hand, the curve for the production of propylene has flattened noticeably, particularly since about 1960 (22), (23), (24). A similar development is to be seen at present in nearly all countries of Europe (55).

Most of the ethylene (36.5 per cent of the production of the western world) is required for the making of polyethylene. Then follows the generation of ethylene oxide (19 per cent of ethylene) used for the manufacture of a number of products such as glycols, amines, detergents and softeners. The production of ethyl alcohol consumes 10.5 per cent, styrene 8.5 per cent and acetaldehyde 3.5 per cent of the ethylene. The halogen derivatives are used as solvents, and dibromoethane is utilized as an addition to tetraethyl lead.

A new branch of industry consuming high rates arises in the future for othylene with the synthesis of vinyl

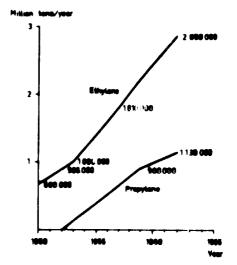


Figure XIII. Production of ethylene and propylene in the United States of America

chloride, starting from ethylene and chlorine and the pyrolysis of dichlorethane. This branch of industry consumes 4.5 per cent of the production of western Europe and the United States of America, (41).

Higher alcohols manufactured from ethylene are intermediates for the production of softeners and surfactants. If the n-alkylary sulphonates should turn out to be insufficiently degradable in the future, the straight chain alcohols with more than twelve C-atoms will gain in significance. Apart from the n-paraffins and natural fatty acids, ethylene represents one of the raw material sources.

Last but not least, mention should be made of the synthesis of alpha olefins from ethylene. The ethylene consumption for their production, however, is relatively low (54).

In point of quantity, propylene takes second place. It is used mainly for the synthesis of isopropanol. Then follow propylene trimer and tetramer as intermediates for the generation of detergents, polypropylene, propylene oxide, cumene, glycerine, n- and isobutanol by oxosynthesis (53), isoprene and acrylonitrile (25), (26).

A new range of applications arises for propylene from the disproportionation reactions. Thus it is possible for instance to form one molecule of ethylene and one molecule of butylene from two molecules of propylene. This interesting reaction is not at all limited to propylene but is applicable to straight chain olefins of up to 8 C-atoms (27).

Of the  $C_4$  isomers, isobutylene is the basis for butyl rubber (polyisobutylene), diisobutylene and isoprene. Further, it is used to produce isoamylalcohol by hydroformylization and to generate tertiary butyl alcohol by means of hydration.

Normal butane and normal butene, which are obtained as by-products from all thermal processes for the production of ethylene and propylene, are dehydrogenated to butadiene. In view of the variety of raw material available for the making of olefins, the design of a plant to be eracted will mainly depend upon the nature of the raw material to be used. The raw materials available are indicated below.

Refinery gas which, apart from hydrogen, methane. ethane and propane, contains about 5 to 8 wt. per cent of ethylene and approximately 0.5 to 1.5 wt. per cent of propylene. A refinery with a catalytic cracking plant and recovery sections for LPG, motor fuel and light and heavy fuel oils, supplies about 3 to 4 per cent refinery gas referred to the crude oil charge. The ethylene production amounts to approximately 0.2 to 0.4 per cent of the crude oil throughput. It can be increased by thermal cracking of ethane and propane to about 0.8 to 1.3 per cent. The ethylene concentration in the gas stream routed to the gas separation plant is increased thereby, and the recovery process becomes a more economical one. So the production costs for the recovery of ethylene from refinery gases are coming nearer to those for the production in a pyrolysis plant.

The investment costs for ethylene plants, expressed as DM/t ethylene, noticeably decrease above a capacity of 150 tons of ethylene per day. To ensure a production of this rate from refinery gases, the refinery must have a crude oil throughput of at least 12,000 to 18,000 t/day or 4 million to 6 million tons a year.

Further sources for the making of olefins are ethane, propane and butane, as well as the gasolene contained in natural gas.

Light gasolene fractions as they are obtained in all refineries have become increasingly important in the past for the production of olefins, particularly in Europe. The point is that the capacity of nearly all European refineries is below the four-to-six-million-tons limit. These fractions are not wanted for motor fuel because of the high demand for the octane number. Furthermore, their conversion to useful motor fuel components with the required volatility presents difficulties. Accordingly these light gasolenes have a low market price and are most suitable for the production of olefins.

Finally, mention should be made of crude oil or its Sec heavier distillates as raw material source. Crude oil as raw material is of interest for all those countries which have only low refinery capacities or in which natural gas is found that, apart from methane, does not contain any higher homologs.

#### Cracking processes

With regard to the raw material, the cracking processes can be divided into two groups.

(a) Cracking of low boling hydrocarbons such as ethane, propane, butane and straight run distillates with FBP's of up to 200°C

At high temperatures and short residence times the thermal cracking process has made its way against the catalytic cracking process at lower temperatures. It is obviously difficult here to maintain the activity and selectivity of the catalyst.

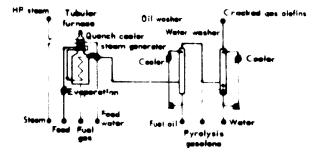


Figure XIV. Principle of tubular furnace pyrolysis naphsha food

Of all types proposed by now for the continuous thermal cracking of light hydrocarbons, the tubular reactor, hereinafter called steam cracker (see figure XIV) has been used more than all (30).

Pyrolysis is carried out in the presence of steam to reduce the partial pressure of hydrocarbon vapour and to avoid coke deposits. The tubes are heated externally to bring the vapour mixture to reaction temperature and to introduce the reaction heat necessary for pyrolysis into the system. The arrangement of the tubes is such that an extremely high utilization of energy of the heating medium and a continuous increase in temperature are ensured. There is some limitation with regard to the residence time, running in the order of 0.6 to 1.3 secs. in virtue of the rate at which heat can be transferred to the reactant.

The interdependence of residence time and reaction temperature at a given cracking degree is illustrated for the ethylene generation from ethane by figure XV (28). For the residence time of 1 sec. and a conversion degree of 60 per cent, the reaction temperature is about 760°C. If the reaction time is reduced to 1/10 second, the tempelature must be increased at the same conversion degree to 840°C.

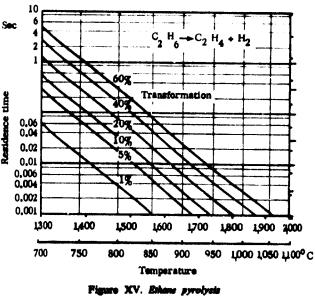


TABLE 11. PURCLYSSE OF STRANSWE RUN DISPUBLICATED



Figure XV1. Model of a plant to produce olefine from naphthe and propane

The tubular furnace is limited in virtue of the temperature resistance of the tube material, the heat transfer effect and the reaction velocity. The pyrolysis, which is carried out at temperatures of about 700 to 800°C, is followed by the cooling of cracked gases. A rapid cooling of the gases at the furnace outlet is necessary to avoid olefin losses by secondary reactions. This is required particularly if a maximum ethylene yield and equilibrium approximation are desired. By means of cooling in a waste heat boiler and subsequent quenching by means of hot water or oil, the cracked gases are cooled down to approximately 180 to 200°C.

Thence, the cracked gases are further cooled, and the heavy hydrocarbons obtained from pyrolysis and the steam added in the furnace are condensed off. The cooling process is carried out on a direct basis (see

TABLE 10. PYROLYSES OF ETHANE, PROPANE AND BUTANE IN TUBULAR FURNACE

	Feedera	)ck		Ethane	Propane	Butane
Operation dat	ia:					
Outiet (°C)	• • • •	<b></b>		830	84.0	800
Outlet (kg/sq.c	m.abs.).			1.2	1.7	1.5
Steam/hydrocs	rbon (m	ole/moie)	• • • •	0.3	0.4	0.35
Conversion (p	er cent)	••••		58.8	87.7	90.5
Cracked gas	Food- stock	Cracked gas	Feed stock	Cracked 848	Feed stock	Crackee 843
Composition (n	nole per (	cent)				
С,Н,	0.3	33.1	1.7	25.4		24.4
CH.	99.3	26.7	11.5	10.3		5.7
С.Н.	0.2	0.6 *	2.1	8.2		11.5
С.Н			84.6	6.0	6.5	1.8
C.H	-				93.5	4.2
<b>C</b> <sub>6+</sub>	_	0.3		1.3		3.6
Others		39.3		48.8		48.8

· Including C.H.

Frederick	S.R. Distillate 32 to 102°C	5.8 Dissillate 190 to 220*(*
Operation data		
Outlet (°C).	766	762
Outlet (kg/sq.cm.abs.)	2.1	2.1
Steam to feed ratio (mole/mole)	75	8.2
Composition of cracked gas		
$C_{s}H_{4}$ (wt. p. cent)	27 2	22.0
C2He (wt p cont)	5.1	2.5
C <sub>a</sub> H <sub>a</sub> (wt. p. cont)	13.2	11.9
C <sub>3</sub> H <sub>8</sub> (wt. p. cent)	0.9	0.4
C4H6 (wt. p. cent)	4.1	4.2
$C_4H_8$ (wt. p. cent)	7.3	5.3
CeHie (wt. p. cent)	0.4	0.3
C <sub>b+</sub> up to i90°C (wt. p. cont)	17.8	30.5
Fuel oil and carbon (wt. p. cent)	8.4	10.5
Others (wt. p. cent)	15.6	12.4

figure XIV) to remove the condensation heat rapidly and to equate the gas temperature with the cooling water temperature as much as possible. The circulating water and the oily condensate are separated in a separator. The water is then recooled indirectly and returned to the cooling tower.

Figure XVI shows the model of a plant which is under commission to produce 35,000 t/year of ethylene and 20,000 t/year of propylene from propane. Tables 10 and 11 show some typical examples of ethylene production, starting from ethane, propane, butane and straight run distillates (29) (see also 23).

The yield of ethylene from the cracking of ethane on a once-through basis amounts to 47 per cent at a cracking degree of 58 per cent. At a cracking degree of about 87 per cent, 28 wt. per cent of ethylene and 17 wt. per cent of propylene are obtained from propane. At a conversion of 90 per cent of butane, the yield of ethylene amounts to 36 to 37 wt. per cent and of propylene 21 to 22 wt. per cent.

Table 11 shows that apart from ethylene and propylene, considerable rates of pyrolysis gasoline of a boiling range of up to 190°C are obtained from naphtha thermal cracking. The rate obtained — as can be gathered from both the examples — depends upon the boiling range of the raw material as well as upon the cracking conditions. In any case the pyrolysis gasoline is rich in aromatics, which can be recovered as already described above. The rate of aromatics is not inconsiderable and amounts to approximately 10 to 12 wt. per cent of the charge for lighter gasolene and about 18 to 20 wt. per cent for heavier gasolene.

In view of the fact that the market is not able to absorb any propylene rate whatever — as can be seen from figure XIII — and that the demand for ethylene is continuously increasing, efforts are made to reduce the propylene generation to a certain degree. The result is a preferred ethylene production by means of high-temperature short-residence pyrolysis or recycling of ethane and propane, which is obtained by hydrogenation of propylene.

#### (b) Cracking of high boiling hydrocarbons

In the case of these raw inaterials, heat is transferred indirectly by means of solid heat carriers. i.e., heat may be transferred by fixed carriers, Onia process, (31) or by moved carriers (31), (32).

It is obvious that the continuous cracking processes with moved carriers will have more significance in the future than the semi-continuous processes with fixed heat carriers.

In the case of the Lurgi-Ruhrgas Sand Cracker (33) (see figure XVII), hot sand is routed to a fluidized bed, where the hydrocarbons to be cracked are injected together with superheated steam. By means of evaporation and cracking the sand is cooled down by about 100°C. As much sand as is fed is withdrawn continuously from the fluid bed. In the lift the sand is heated up directly by flue gases and routed to the collecting bunker. The carbon formed during cracking is burnt off here. The heat of the flue gases is utilized in the heat exchangers to heat up the steam, the air used in the process as well as the feedstock.

After they have passed a cyclone in which the entrained sand is separated, the cracked gases are quenched and cooled down in a similar way as in the steam cracker.

Five plants utilizing this process for cracking of naphtha or crude oil are now under commission or construction. Together they have a capacity of 160,000 t/year of ethylene and 75,000 t/year of propylene.

A further fluidized bed process has been developed by Badische Anilin- und Sodafabrik AG particularly for the cracking of crude oil (31), (34).

The process makes use of the coke obtained from cracking or uses a temperature and wear resistant granular material as heat carrier. Two types of process are basically possible for meeting the demand for heat supply, i.e., the carrier is continuously removed from the fluid bed and heated up outside the reactor, or the heat necessary for evaporation and cracking is obtained from a burning process taking place in the reactor by introduction of oxygen. In this case the cracked gases are diluted by the combustion gases. This type of process is

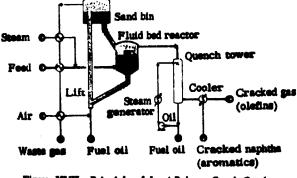


Figure XVII. Principle of Lurgi-Rulegas Sand Cracker

of particular importance if the cracking plant can be combined with a synthesis plant, e.g. methanol or ammonia synthesis.

**BASF** process and sand cracker are also suitable for the cracking of light hydrocarbons. Both processes supply high rates of aromatic-rich pyrolysis gasolenes. By quenching the hot cracked gases with naphtha the pyrolysis gasolene output can be increased in some cases up to 100 wt. per cent referred to the ethylene generated. The aromatics content of the pyrolysis gasolenes generally ranges slightly above 60 per cent.

Compared to the steam cracker, BASF process and sand cracker are more flexible with regard to the feedstocks and are less limited to severe cracking conditions. The propylene portion can be repressed by this means in favour of a higher ethylene yield. Thus, in the case of butane cracking (29) in a reactor with moved heat carriers, the ethylene yield can be increased up to 45 wt. per cent by raising the cracking temperature at a propylene generation of 12 wt. per cent, whereas in the steam cracker only 30 to 35 wt. per cent of ethylene are obtained at a propylene generation of 21 to 22 wt. per cent.

For the sake of completeness mention must be made of the processes of high-temperature pyrolysis of hydrocarbons. They are suitable for the production of both acetylene and olefins by pyrolysis in a range of 1,300 to 1,700°C. The heat necessary for pyrolysis is generated by the burning of hydrogen, methane or other fuel gases. The hydrocarbons to be cracked are mixed with the hot flue gases, and the reaction mixture is rapidly cooled down after the reaction path (35). Thence, the acetylene is removed from the cooled cracked gas, and ethylene as well as propylene are recovered from the remaining gases.

The cooled cracked gases from steam crackers, sand crackers and fluid bed processes, e.g. BASF process, are now separated in a gas separation plant into pure hydrocarbons or their fractions. As the specifications for pure ethylene and pure propylene are extremely high, combinations of chemical treatment, drying, superfractionation and hydrogenation processes are used to process the cracked gas mixture. Three types of process are basically possible (29):

(a) Processes which operate at low pressure and low temperature following the well known air separation plants at temperatures down to minus 180°C;

(b) Processes which use medium pressures of 25 atm. and medium temperatures of about minus 40 to minus 60°C, with ethylene being generated by absorption;

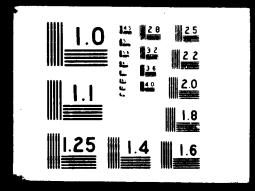
(c) Processes which operate at medium pressures up to 35 atm. and low temperatures down to about minus 130°C, following the distillation technique of refineries.

The process of such a plant, using pressures up to 35 atm. and temperatures of about minus 130°C, is described below (see figure XVIII).

To achieve a distillative separation, the pressure of the gases from the cracking plant must be increased so that the major portion of the gas can be liquefied. The compression is carried out in four stages. The design and selection of the compression stages have been accomplished under the particular consideration that the heaviest

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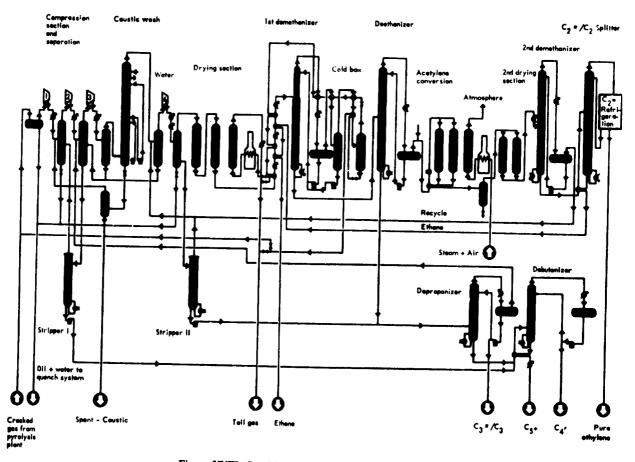


Figure XVIII. Simplified flow sheet of gas separation plant

hydrocarbons of the cracker gas, which tend to gum formation, must be removed before the gas is further processed. Moreover, high temperatures in the compressor plant must be avoided to minimize the danger of polymerization of the heavy unsaturated hydrocarbons in the cracker gas.

The process gas is intercooled after each compression stage. The components which condense in the intercoolers are collected in the respective separators. The condensate from the first stage separator is returned to the oil/water separation unit arranged in the quench system of the pyrolysis plant. The condensate from the third stage is flashed into the separator located after the second stage. The liquid product from the separator is passed to stripper I to remove the lower boiling components. Thence, it is passed to the low pressure debutanizer. When cooling after the fourth stage, a considerable portion of the C<sub>a</sub> hydrocarbons is already removed by condensation. This condensate is passed to stripper Il. In the stripper the C<sub>a</sub> hydrocarbons contained in the condensate are removed and returned to the fourth stage. The bottoms product, mainly consisting of C. hydrocarbons, is supplied to the depropanizer.

Between the third and fourth compression stage the process gas is passed through a caustic washer. This washer system, which is required to remove sulphur compounds and CO<sub>2</sub>, comprises a double-stage caustic washer and a subsequent water washer.

Before entering the low temperature section of the distillation plant, the process gas already compressed to about 35 atm in the compression plant is dehydrated by absorption of the major portion of water on activated alumina. The three dehydrating units are operated in such a way that the gas can always pass through two of them, whilst the third is being regenerated by the dry and hot residual gas stream from the demethanizer. The last regenerated unit of the two operating ones is connected after the other unit, which is more heavily loaded so that an optimum dehydrating action is achieved.

The gases from the dehydrating plant are cooled in a condenser group by cold residual gas and partly condensed by an evaporating refrigerant. Thence, the gases are passed to the demethanizer tower to be split into ethylene and heavy hydrocarbons (bottoms product) and into hydrogen, methane and a small portion of ethylene (overhead product). From this overhead product the major portion of ethylene component is recovered in a subsequent condensing and flashing system by utilizing the Joule-Thomson effect. The recovered, contaminated ethylene/ methane mixture is returned to the demethanizer.

In the first deethanizer tower the  $C_1$  hydrocarbons (ethylene and ethane) from the bottoms product of the

first demethanizer tower are removed overhead. The bottoms product of the deethanizer, which consists of  $C_s$  hydrocarbons and heavier components, is passed to the hot section of the plant for further processing. Together with the liquid stream from the compressor unit (bottoms product of stripper II), it is fed to the depropanizer.

The overhead product from the first deethanizer (ethylene/ethane mixture) contains a small portion of acetylene which must be removed so that only traces will remain in the pure ethylene. This is achieved by means of selective hydrogenation in an acetylene converter unit where the acetylene is converted partly to ethane and ethylene. This conversion takes place at higher temperatures over a noble metal catalyst. The hydrogen required for this purpose is obtained by a 70 per cent hydrogen injection into the process gas stream entering the reactor. The hydrogen gas is taken from the flashing stage after the first demethanizer. Since small rates of ethane, methane and hydrogen will penetrate into the process gas stream by the acetylene converting process, the acetylene removal is performed before ethylene is finally separated from its contaminations. On the other hand, the conversion process shall take place on an ethylene stream which is as highly concentrated as possible so as to ensure that the specified product quality shall be obtained.

The process gas from the acetylene converters is cooled and partly condensed in heat exchangers and then passed to the second demethanizer tower. Thence, the methane not entirely removed in the first demethanizer and the excess hydrogen injected upstream of the acetylene converters (including the methane mixed to the process stream with the contaminated hydrogen) are removed overhead. This overhead stream contains a certain amount of ethylene which is recycled to the fourth stage of the feed compressor so that its ethylene content is not lost.

The ethylene/ethane mixture from the bottom of the second demethanizer is separated in the ethylene/ethane separating tower into pure ethylene and ethane. To produce the necessary reflux, the heat pump principle is applied, i.e., the overhead vapours are compressed by the compressor of the ethylene refrigerating plant, and the reflux stream is condensed in the reboiler of the tower. The pressure of the ethylene vapour is simultaneously increased in the ethylene refrigeration plant from the tower operating pressure to the discharge pressure.

The bottoms streams from the first deethanizer and stripper II are introduced together into the depropanizer. In the depropanizer the streams are split into a propylene/ propane mixture (overhead product) and into a mixture of  $C_6$  and heavier hydrocarbons (bottoms product).

The bottoms product from the depropanizer consists of  $C_4$  hydrocarbons and higher boiling components. A further stream of heavy hydrocarbons is obtained as bottoms product from stripper I of the compressor unit. These two streams are fed to the debutanizer and split into a  $C_4$  stream and a bottoms stream consisting of pentane and heavier hydrocarbons. The propylene and ethylene refrigerating plants serve to produce the temperatures required for the process.

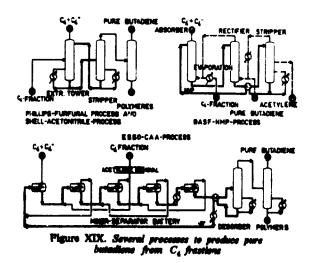
Both these plants comprise a four-stage compressor unit each, including the required intermediate drums and coolers for the condensation of the evaporated and recompressed refrigerant. The intermediate pressures are selected as required for the various refrigeration levels.

The compressed refrigerant vapours are condensed after the fourth stage in the propylene refrigerating plant by means of cooling water. The condensation in the ethylene refrigeration system is achieved by propylene. A part of the power required to produce the icw temperatures by means of ethylene is obtained from the propylene refrigeration plant of the cascade type.

The propane/propylene mixture from the gas separation plant contains acetylene derivatives, the concentration of which depends upon the cracking conditions. These derivatives must be removed since they are inconvenient for the subsequent treatment of propylene. The removal or conversion is carried out by selective hydrogenation in the gas phase (38) or in the liquid phase (36). Thence, they are fractionated to recover pure propylene.

The same applies to the  $C_4$  fraction (37). The  $C_4$  fraction from the gas separation plant contains about 20 to 40 per cent of butadiene as its most valuable component. The most important processes for its separation are shown in figure XIX.

The oldest among these processes is the Esso-CAA process, shown in the lower section of the figure. It works to the liquid-liquid extraction principle with a copper ammonium actate solution and uses the ability of the copper-tetramine complex to bond butadiene at low temperatures and set it free at higher temperatures. The solvent is precooled to minus 20°C and passed through a mixer separator battery. After removal of the acetylene compounds, the C<sub>4</sub> fraction is introduced at about the centre of the extraction line. The right section of the extraction battery serves as rectifier, i.e., pure butadiene is passed towards the saturated solvent so that the butenes, which are dissolved in addition to butadiene, are displaced by butadiene. The reflux is obtained by heating up the saturated solvent before the



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last separator, thus liberating a portion of the dissolved butadiene. The remaining  $C_4$  hydrocarbons leave the first separator, whereas butadiene is separated from the solvent in the desorber. In the subsequent tower small rates of high boiling impurities arc separated.

The Phillips process (see upper left section) uses the principle of the extractive distillation with furfural as extraction solvent. Butadiene leaves the bottom of the left tower together with furfural and is distilled off from the extraction solvent in the stripper. The final purification is carried out in the right tower.

The Shell process (39) uses the same principle but substitutes furfural for acetonitrile. The advantage of acetonitrile is its better extractability, i.e., the process operates more economically.

Contrary to other processes, the BASF-NMP process (40) works according to the gas washer principle. N-methylpyrrolidone, which is utilized as solvent, ic also used in other absorption and extraction processes. Butadiene is selectively separated in the absorber. Small rates of butene are also dissolved and stripped off by a countercurrent of pure butadiene in the rectifier.

The acetylene compounds, which have the greatest affinity to the solvent, are withdrawn in gaseous state from the lower section of the stripper. This process is particularly suitable for the treatment of  $C_4$  fractions with a high acetylene content. Hence, the prior removal of acetylene is not required.

It is not easy to give a survey of the costs for the production of olefins. The cost price for one ton of olefins depends upon many factors. Let us start with the raw material. First, the olefin yield depends upon its boiling range. Paraffin base raw materials of necessity result in higher ethylene yields and concentrations in the cracked gas than naphthenic base raw materials. Hence, the raw material is decisive for the basic design of the tubular furnace and gas separation plant and thus for the extent of investments which are higher for naphthenic base raw materials than for paraffin base ones.

Further, the raw material cost and the valuation of the by-products, such as propylene, pyrolysis gasoline, butene and butadiene, obtained in addition to etilylene from the cracking process, represent decisive factors. The consumption of energy and the purity required are the most important factors for the selection of the gas separation process.

In general, the investment costs for a steam cracker plant, comprising furnace section, gas separation section with hydrorefining of ethylene, ethylene-ethane separation, ethane recirculation and generation of an unrefined propane-propylene fraction as well as a  $C_4$  fraction, referred to one ton per year of ethylene, are as follows:

Ethylene production . . . . 50,000 t/year 100,000 t/year DM invested (ton/year ethylene) 520 to 600 400 to 470

One-third of the investment costs are required for the furnace section, and about two-thirds refer to the gas separation plant.

The production costs must be calculated separately for each individual project as the prices for energy and naphtha depend mainly upon the local conditions. Further, the economic analysis includes the proceeds for the by-products. The extent of influence of the byproducts on the economics may be gathered from the following summary.

To produce 1,000 kg of pure ethylene, approximately 3,500 kg of naphtha with a boiling range of 40 to 200°C are required. Taking into consideration all losses, the pure ethylene yield in the case of ethane recirculation amounts to 28.5 to 32 per cent. In addition, 450 kg of a propylene/propane fraction (acetylene-bearing, 90 to 95 per cent propylene content), 340 kg of a C<sub>4</sub> fraction, 1,100 kg of pyrolysis gasoline and 610 kg of fuel gas, preferably hydrogen and methane, are obtained.

Considering the cracking plant alone, the investment costs for a sand cracker are slightly higher than those of a stram cracker of the same capacity. However, as the major portion of the investment costs refer to the gas separation plant, the over-all costs are only a little higher than those for a combination steam cracker/gas separation plant. The same applies also to the operating costs. In this context, mention should be made again of the flexibility of the sand cracker, which can process all hydrocarbons from ethane up to crude oil.

The above-mentioned prices are calculated on the basis of European conditions, with the olefin plant being built as part of a refinery. The prices do not include licences, know-how fees and financing costs.

### **PARAFFINS**

A decade ago, straight chain paraffins could be processed commercially only by means of the Fischer-Tropsch synthesis, the conversion of carbon monoxide and hydrogen. Now the South African Gas and Oil Corporation, Sasol, at Sasolburg, South Africa, is the only firm making use of this process. This factory was built during ibe years 1952 to 1955 through the co-operation of the M. W. Kellogg Company, New York, Ruhrchemie AG, Oberhausen and Lurgi Gesellschaft für Wärmetechnik mbH, for the Union of South Africa. On the basis of coal with a high ash content it produces petrol, diesel oil, and slab and hard wax. The Fischer-Tropsch process therefore supplies a variety of hydrocarbons, from methane to high molecular wax.

In its activity to keep the rivers clean by means of placing biologically degradable detergents at the disposal of the population, the petrochemical industry was confronted with the problem of supplying high rates of straight chain hydrocarbons of the  $C_{10}$  to  $C_{14}$  and  $C_{10}$  to  $C_{17}$  range as coupling components.

As with aromatics, petroleum was able to fill the raw material gap. In the boiling range of 170 to 270°C (see figure XX), the necessary straight chain hydrocarbons are contained in the straight run distillates of petroleum. Because of the variety of isomers a separation of the straight chain paraffins cannot be carried out by means of conventional methods. Here we can make use of inolecular sieves, synthetic aluminium silicates, with exactly defined pore sizes as absorbents (42, 43), which even under operating conditions maintain their proper size.

The following properties of the molecular sieves are of interest for the technical process: they only catch those

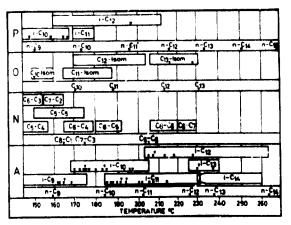


Figure XX. Boiling points of paraffins, olefins, naphthenes and aromatics at 760 torr.

niolecules that are smaller in diameter than the pores themselves; they adsorb olefins better than paraffins and they preferably adsorb paraffins with higher molecular weight.

The outcome of the mixture under treatment is that the fraction to be processed is not cut too extensively and probably does not contain any olefins. Furthermore, the molecular sieves require a raw material which is free from any gum whatever. In so far as the final product is concerned, exacting demands are made on the sulphur and nitrogen content by virtue of its final utilization as detergent.

Therefore, the straight run distillate must be subjected to hydrorefining before the n-paraffins are separated. The olefins are saturated to paraffins, and the sulphur, nitrogen and oxygen compounds are hydrogenated to hydrocarbons under removal of hydrogen sulphide, ammonia and water. The raw material is then dehydrated to remove the last traces of water.

Adsorption on molecular sieves is an equilibrium process. That is, the rate and extent of adsorption depend on the concentration of the straight chain compounds in the fluid surrounding the sieve and on the amount of the compound which is already in the pores of the sieve. Since the rate of adsorption tends to level off as the sieve approaches saturation, it is generally preferred to load the sieves up to a point which is appreciably less than saturation.

The adsorbed meterial can be recovered from the sieve by heating or by applying vaccum. The adsorbed material can also be eluted from the sieve by exposing the sieve to another adsorbable but lower boiling hydrocarbon. Thus, the normal  $C_{10}$  to  $C_{17}$  paraffins on a molecular sieve can be recovered by passing n-hexane over the sieves and recovering a mixture of n-hexane and  $C_{10}$  to  $C_{17}$  n-paraffins. Distillation of this mixture would then yield n-paraffins and n-hexane for use in the next desorption cycle.

We know of the following commercial processes which are different with regard to the adsorption and regeneration conditions, not limited to the  $C_{10}$  to  $C_{14}$  range

only, and all of which use molecular sieves of the same pore size (46, 47).

The Isosiv process (44, 45), developed by Linde Company, a Division of Union Carbide Corporation, operates in the vapour phase, and desorption is accomplished by reducing the pressure in the adsorber.

In the Texaco Selective Finishing Process (48), (46), the adsorbed hydrocarbons are stripped off by means of some vapour phase desorption medium. The Enjay Chemical Company process was developed by Esso Research and Engineering Company (40). This process adsorbs the n-paraffins in the vapour phase in a moving bed, whereas desorption is effected at a higher temperature than the adsorption.

The British Petroleum Company (46) has built its first plant in the Federal Republic of Germany to produce 30,000 t/year of n-paraffins by its own process. The engineering was carried out by Lurgi Gesellschaft für Mineralöltechnik mbH. Adsorption in this process takes place from the vapour phase but desorption is accomplished with a low boiling paraffin.

The adsorber, which is filled with molecular sieves, is first charged with the hydrocarbon vapours. The n-paraffins are adsorbed by the molecular sieves, whereas the other hydrocarbons leave the adsorber in a vaporous state and are condensed in a cooling tower. When the maximum load is reached, i.e., shortly before the breakthrough of n-paraffins, the charging is interrupted (see figure XXI). Thence, the adsorber is purged with a low boiling hydrocarbon, which, owing to the existing partial pressure conditions, displaces the formerly absorbed n-paraffins. A mixture of low and high boiling hydrocarbons is obtained here. The low boiling carbons are distilled off from this mixture and returned to the process. The recovered n-paraffins cemain as bottoms product. Now the adsorber is regenerated and then ready to be reloaded.

It should be mentioned that the molecular sieves are loaded under pressure. This is done for economic reasons since the adsorption rate of the molecular sieves, as in the case of all adsorbents, increases more substantially with increasing pressure. In order to avoid cracking, the evaporation is carried out in the presence of nitrogen as carrier gas. The entire cycle is controlled by means of a timing system which is similar to the switch system of an

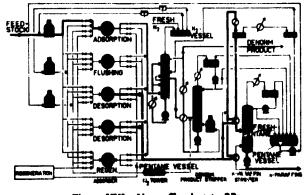


Figure XXI. N-parafin-plant to BP

activated carbon plant to recover solvents --- loading, steam purging, drying and reloading.

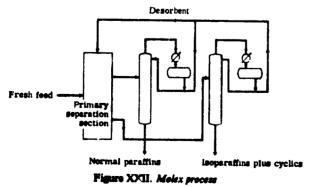
The distillation unit downstreams of the adsorber group is of simple setup since the difference in the boiling points of the desorbent and recovered n-paraffins is great. By means of the parallel connexion of several adsorbers, the discontinuous operation of the single adsorber is converted to a fully continuous one, which, compared to any other solvent recovery plants, is substantially simplified by virtue of elegant designs.

Ine Molex process (49, 50, 51), developed by Universal Oil Products Company, has been selected as the route to detergent-range n-paraffins by Continental Oil for their plant at Lake Charles, La., by Gelsenberg Benzin AG, Federal Republic of Germany, and others. Gelsenberg Benzin AG, was also erected by Lurgi Gesellschaft für Mineralöltechnik mbH.

The process can be described as follows (see figure XXII): separation is accomplished by adsorption of n-paraffins from the liquid phase in a bed of molecular sieves. Operation is isothermal and continuous, in that feed and product streams enter and leave the process at a constant rate and with constant composition. Pressures are moderate, and temperatures do not exceed the atmospheric boiling points of the charge stocks. The system makes it possible to use a single stationary bed of solid adsorbent in a way which produces the desired results.

The desorbent used in the Molex process is a low boiling hydrocarbon fraction. Paraffins with a purity up to 99.2 per cent are obtained. However, as in the case of all adsorption processes, purity, yield and operating costs are interdependent.

Proper treatment of the feed will make it possible to operate for long periods before regeneration of the molecular sieve is necessary, so that onstream efficiency of 90 per cent and a mole. sieve life of over two years can be expected. The following estimate of operating and capital costs for a Molex unit is given (50): for a unit designed to produce 136 cu.m./day of n-paraffins from 710 cu.m./day of a feedstock containing 23 per cent by volume of straight chain molecules in either the kerosene or light gas oil boiling ranges, the total of direct operating costs is estimated to be 0.58 cent per pound of normal paraffins, corresponding to approximately DM 52.--/t. n-paraffins. This figure includes replacement of sieves, chemicals, utilities, labour administration, laboratory



charges, local taxes and insurance, but does not include any allowance for pay-out. The erected cost of this unit including sieves and chemicals is estimated to be 10 million DM. These data are of course subject to the qualifications on costs stated in the preceding paragraph.

In the case of the Isosiv process (46), the costs for a plant of about 160 cu.m. of n-paraffins/day amount to 8.8 million DM, including the initial loading of molecular sieves. No mention is made of the quality of the feedstock or the purity of the n-paraffin product.

Excluding offsite facilities, however, operating costs are said to be about DM 80.—/t. n-paraffins, licence exclusive.

The aforementioned processes are used not only for separation of n-paraffins of a boiling range of 170 to 300°C but also for lew boiling straight run distillates and reformates; on the one hand, to increase the octane number by removal of paraffins and, on the other hand, to recover n-paraffins to be used as fuels for aeronautic purposes. Low boiling n-paraffins are of interest for the chemical industry as raw material for the production of acids, aldehydes and alcohols. The combination of aromatics extraction, molecular sieve and isomerization processes offers interesting possibilities for the future. Cracking of n-paraffins to olefins may also be possible by means of such combinations. We are therefore in the midst of a fast-moving development and there is yet no end in sight.

Two decades ago it was difficult for the chemist to make or buy half a kilogram of pure benzene with a melting point of above 5.50°C. Today, benzene of high purity is being produced in thousand of kilograms per hour.

To recover pure ethylene, sugar had to be fermented to alcohol, which was then dehydrated catalytically. The result was a product regarded at the time as pure ethylene but which would not meet the present specification for pure ethylene at all.

It was a painstaking task for the chemist to produce n-paraffins. By means of distillation it was only possible to obtain pure n-pentane or n-hexane, but not higher homologs. Furthermore, the product yield and purity 'as very low.

The development of the production process would have been hampered if the science of analytical chemistry were not at the disposal of the mechanical and chemical engineers. Today, with the utilization of modern apparatus good results by means of analytical chemistry can be obtained within a very short time, whereas, only a decade ago the same results would have taken several days or even longer to achieve.

The author has tried to give a general view of a field which is of great interest to the scientist and the engineer, and to the businessman as well. We have learned that petroleum has surpassed or replaced coal, the original basis for the production of basic materials for the organic chemical industry.

It is almost impossible to give a forecast of the coming development in the field of petroleum chemistry. Doubtless, however, we are in the midst of an evolution, the end and extent of which cannot be foreseen.

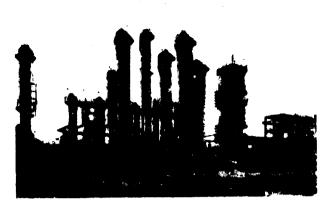


Figure XXIII. Arosolvan plant to produce pure benzene, pure toluene and xylene



Figure XXIV Areasolvan plant to produce pure benzene and pure toluene



Figure XXV Sand cracker to produce olefine



Pigners XXVI. Plant to produce n-paraffer

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### 8. APPLICATION OF ADVANCED TECHNOLOGY TO DEVELOPING COUNTRIES FOR BASIC PETROCHEMICAL INTERMEDIATES

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### INTRODUCTION

This paper presents a general discussion of the application of petrochemical industry technology to developing countries, illustrated by certain specific basic intermediates. By basic intermediates, are meant chemicals which are required for the production of consumer products such as fibres, plastics, and detergents, but which must themselves be derived from basic raw materials such as petroleum. The basic intermediates selected for discussion are those which have the largest scale of application today to the manufacture of the consumer products to be discussed in subsequent papers.

This paper discusses first, in broad terms, the benefits of advanced technology, as illustrated by the experience of the petroleum industry. It then discusses in some detail the problems and costs associated with the transfer of technology to developing countries, and the differentials compared to developed countries. This general discussion concludes with a consideration of the way in which the cost data given in the literature should be applied when planning for a developing country.

The next section discusses several of the important basic intermediates. Ethylene is featured, not only because it is one of the most important and rapidly growing petrochemicals, but also because the data available permit intensive examination.

Problems in the developing countries are illustrated by a brief discussion of experience and current trends in South America. The paper concludes with an appraisel of the means available to developing countries for gathering and interpreting the data needed for their planning activities.

### BENEFITS OF ADVANCED TECHNOLOGY

The purchase of advanced technology is a necessity for developing countries, and often the initial cost appears high. But it is the over-all costs that are the true indication, and there is no doubt that a developing country will benefit from the reduced costs of manufacture that result from the application of the advanced technology.

It is revealing to consider the experience of the petroleum refinery industry, as reported in a recently published study by the Esso Research and Engineering Company.<sup>1</sup>

Costs were estimated for the completion of "grass roots" refineries built during the period 1937-1957, and were adjusted to 1957 dollars to eliminate the effects of money inflation. The study showed that during the period 1944-1957, improved technology had reduced manufacturing costs to such an extent that the 1957 costs were half of the i944 costs, and that the subsequent trend had been a cost reduction of 5 per cent per year.

Admittedly, 1944 was a high point reflecting the wartime demands for aviation gasolene, but when the war ended, the research effort was directed towards reducing manufacturing costs and improving product quality. Technological advances permitted the building of larger capacity units, as much as four times the pre-war capacity, which naturally tended to reduce manufacturing costs. But other equally important advances reduced the investment and operating costs for any given capacity, and also increased the flexibility of the units with regard to the range of feed stocks, operating conditions, and product specifications. Studies of unit efficiency showed that small capital expenditures to remove "bottlenecks" would sharply increase the maximum capacity, and this knowledge was applied to the design of subsequent units.

It is certainly true that these experiences will be, and are being, repeated with the basic petrochemical plants discussed in this paper, and the implications for the developing countries are several. First, the investment cost of improved technology may be high, but the production cost of inadequate technology may be prohibitive. Secondly, when the technology has been purchased and is in operation, there are additional dividends to be gained by well-planned investigations of plant operating efficiency and incremental investment to eliminate bottlenecks and reduce operating costs.

### PROBLEMS AND COSTS ASSOCIATED WITH TRANSFER OF TSCHNOLOGY

The major kinds of differentials in capital and operating costs that can apply to a transfer of technology to a developing country are outlined in table 1 (p. 285). Some general qualifications should be made immediately. First, the table is illustrative and is not put forward as being comprehensive. Secondly, not all the items listed will apply to any given plant in a developing country, but some will apply to most plants in most countries. Thirdly, the items are applic, ble to all kinds of plants, and not only to the basic intermediates, which are the

<sup>&</sup>lt;sup>1</sup> R. A. Cardello and G. D. Ward, Chemical Engineering Progress 60 (2):85-88 (July 1964).

subject of this paper. But the quantitative effects will vary significantly with the individual petrochemical and country.

As regards the table, it may be asked what is meant by an "inside battery limits" process unit, which is taken as a base point of reference. The term grew from petroleum refinery practice, where a large number of individual process units are required to make the full range of products. The physical boundaries of each such unit are known as the "battery limits", and it is well understood in refinery practice that all supporting facilities such as feed and product tankage, electrical generation, water systems, inter-connecting piping, surrounding roads, all buildings except the control house, etc., are considered to be "outside battery limits." These terms have such general acceptance that they are used as initials, i.e. ISBL and OSBL.

The important characteristic of any ISBL unit is that it is not completely self-sufficient, since it requires a certain minimum of OSBL supporting services. The extent of these facilities will depend not only on the unit itself, but also on the other process units with which it is associated, since some integration of mutual benefit is always possible. Since cost and input data for a process are nearly always given in terms of an ISBL unit, the total actual requirements for a developing country are rarely covered by such data.

### Differentials in capital cost for same scope

### Licences or know-how fees

These costs are incurred by the developing country to acquire the advanced technology, with resultant benefits as discussed previously. They are included as a differential cost since, at present, developing countries rarely have any other means of obtaining technology. The costs may amount to from 0 to 5 per cent of the ISBL unit cost.

### Shipping costs

The magnitude of these costs will vary with the country, but may amount to from 5 to 15 per cent of the ISBL cost.

### Construction costs

United States chemical companies have been constructing and operating chemical and petrochemical plants in foreign countries for a number of years and some of their experience has been published in detail.<sup>a</sup> Some of their observations pertinent to this paper are given below:

1. Most kinds of equipment cost less in Europe than in the United States of America. For items manufactured in developing countries such as Mexico and Brazit, the costs are often equal to or greater than the costs in the United States.

2. Materials (steel, electricals, pipe, insulation, etc.) costs in Europe are approximately 75 per cent of the

prices in the United States of America, but costs in other areas are equal to or greater than prices in the United States. They are much higher than the relative manufacturing labour rates would indicate.

3. Fringe benefits for labour abroad are much broader than for the United States of America, and their cost represents a much higher percentage of the base rate.

4. When corrections are made to the direct construction labour rates for length of work week, mechanization and job duration, the equivalent field construction costs become equal to or exceed the costs in the United States, for most countries.

5. Elapsed calendar time for design, procurement and construction is significantly greater for small plants (value less than US \$1 million) and somewhat greater for larger plants.

6. The use of indigenous materials for construction and operation of the plant is a worthy and legitimate objective for any developing country, but in many cases it is expressed in the form of an inviolable rule. Sometimes such a stipulation may be detrimental to the over-all economics of the project; some typical instances are given below:

(a) Locally manufactured materials may be supplied with variations in quality or analysis which cannot be accepted without jeopardizing the quality of the construction of the plant. For example, steel may not be of adequate quality for pressure vessels or pipe; poor cement or sand may limit the strength properties of the concrete, thereby making concrete structures inadequately designed; and chemicals may not be of suitable quality. Sometimes these differences can be remedied but with a resultant delay in delivery or a premium in price; sometimes, however, the local manufacturer cannot justify raising his quality merely to satisfy one customer.

(b) The supply is not adequate for the peak demands of the construction period. This is often true for common building materials because a major process construction project may require much more material in a given time than, say, ordinary commercial buildings or ordinary civil projects.

7. The aggregate effect of the equipment, materials and labour costs relationships is that the total capital costs for construction overseas amounts to from 120 to 140 per cent of the costs in the United States of America, depending upon the extent of use of premium-cost indigenous capital equipment. This conclusion is valid only for the same scope of plant; elsewhere in this paper, it is pointed out that some increases in scope may be required for developing countries.

### Differentials in capital cost for increased scope

### Spare equipment

In a developing country, the penalties for plant shutdown are usually severe, because the plant may well be the sole source for the country. For this reason, additional investment is justified for installed or warehouse spare equipment so that continuous production can be maintained. Similarly, because the source of supply is

<sup>&</sup>lt;sup>4</sup> H. C. Bauman, Industrial and Engineering Chemistry, 54:34-38 (July 1962).

remote, and because vendor service is important, additional investment is justified to standardize certain types of equipment, thereby reducing spare parts inventory. The incremental cost for spare parts may amount to from 2 to 5 per cent of the ISBL cost.

### incremental feed and product storage

The need and justification for incremental storage are apparent from previous comments. The additional cost may amount to from 5 to 10 per cent of the ISBL cost.

### Maintenance facilities

In a developing country, there often are no major public shop facilities, as there usually are in large industrial centres. Therefore, the plant must be mainly self-sufficient.

### Marine facilities

Similarly, there is often no established port and the plant must develop and construct its own.

### Housing and commissary

Plants are often built in undeveloped areas where the need for housing and a commissary is obvious. In developing countries, however, housing may be in extremely short supply even in urban areas and it is often necessary for the plant to build and run a small residential colony for its supervisory, technical and production personnel.

The incremental cost for the aggregate of maintenance, marine and housing facilities may amount to from 10 to 30 per cent of the ISBL unit cost.

### Recruitment and training

Because manpower skilled in the operation of a process industry is usually scarce, it is often necessary to recruit operators, foremen, supervisors and managers well in advance of the plant start-up date, and to embark upon an intensive training programme. This will include classroom instruction and possibly direct plant experience in a foreign country.

### Commissioning and start-up

In such a case, the commissioning and start-up of the plant are an extension of the training programme and may take longer than if skilled personnel were already available. Furthermore, foreign technicians and advisers may be required for an extended period of time until the trainces are fully ready to perform on their own.

The aggregate cost of recruitment, training and start-up may amount from to 2 to 10 per cent of the ISBL costs.

### Differentials in production costs

There will be differentials in production costs that are a direct result of capital cost increments and a smaller scale of production; in addition, there are several others worth noting briefly.

### Shipping costs for imported raw materials, etc.

Shipping costs for imported raw materials, etc. are difficult to predict but may amount to a 5 to 15 per cent premium above European or United States cost.

### Advisory services

Long-term advisory services from expatriate personnel may be advantageous in certain areas. No valid approximation can be given.

### Use of indigenous utilities and supplies

Indigenous utilities and supplies are often more costly than in Europe or the United States of America because of the small scale on which they are made or because their reliability is uncertain. This burden may have to be borne by the petrochemical plant as increased production costs.

Virtually all petrochemical processes require reliable, economical electric power; and, in developed countries, purchasing power from a central utility power-station is preferable to generating it within the petrochemical complex. The degree of reliability required is high because an upset of a few seconds may result in a complete shutdown of the plant for an appreciable period of time until the plant is again in full production. Frequent shutdowns will not only affect the efficiency of the plant but may also shorten the life of some of the equipment.

Often, developing countries are short of power even for municipal services, and the generation of power within the plant becomes necessary. This is costly, not only because of the small scale, but also because a certain reserve capacity must be installed to permit the starting of individual large motors.

Modern instruments require that the frequency and voltage be held constant within very narrow limits; variations tolerable for municipal light and power may adversely affect the operation of a process plant.

### Initial lower productivity

With a new plant and newly trained personnel, productivity may be lower during the first few months of operation. Skills increase rapidly, however, and there is much evidence to show that developing countries can achieve and maintain good productivity after the learning period is over.

### By-products

Production costs may be adversely affected because there is no local market for by-products or because quality improvement is necessary in order to compete in the international market.

### APPLICATION OF COST DATA

In a subsequent section of this paper, representative cost data for certain petrochemical processes are presented. These data have been derived from the articles published in the technical journals, or from brochures furnished by companies specializing in the field. Ordinarily, these are the sources of data most generally available for preliminary planning. The way in which these data should be applied to the requirements of the developing countries is discussed briefly below.

1. Published data are intended to indicate the economic worth of technical innovations and improvements, and to attract interest from prospective purchasers or licensees. Since it is obviously impractical to offer schemes which are optimum for all situations, the published data tend to select scopes. conditions, and capacities which are favourable to the process. In some cases, since these developments are keyed to the large-scale advanced technology of the United States and Europe, they may be less favourable when adjusted to the needs of a developing country.

2. The plant is usually described in terms of an "inside battery limits" unit, with all the restrictions in scope that we have previously noted.

3. The price will probably be subject to  $\pm 10$  per cent or more variation, depending on the availability of commercial experience for construction costs, and the willingness of the process owner to disclose accurate prices in a competitive market.

4. If the price is more than a year old, some adjustment should probably be made for escalation. Published cost indices show, for process plants, an average increase of approximately 3 per cent per year, compounded.

5. Escalation may be offset or even completely compensated for by advances in technology, especially if the data are several years old. Very old data tend to be unreliable for this reason.

6. The price is given for one capacity, which capacity rarely correponds to the one desired by the user. Costs can be converted to the desired capacity by the use of scaling factors expressed as exponents. Typical exponents and the corresponding arithmetic ratios are given for various exponents in table 2. If no specific recommendation is given in the source article, the use of an exponent of 0.6-0.7 is a reasonable assumption.

Scaling factors are at best approximations and it is not likely that the same scope of plant has been carefully estimated (or built) at a number of different capacities. Scaling factors can introduce uncertainties of as much as 20 per cent, depending on the ratio between the desired capacity and the capacity for which the price is known.

7. Because the developing country will have to import a major part of the equipment, materials and services for the plant, the distribution of total cost between foreign exchange and local currency will be of great importance. Published data rarely provide guidance in this respect, and for preliminary purposes the developing country should assume that a minimum of 70-80 per cent of the cost will have to be in foreign exchange.

8. Similar considerations apply to production costs. Those costs which are a function of investment carry their proportionate share of uncertainty.

The unit requirements for raw materials, utilities, chemicals etc. are usually reliable and are not subject to change for different sizes of plants, but the unit costs may be considerably different for a developing country. Labour and maintenance costs are liable to be higher for a developing country after allowance is made for scale of plant, productivity and lack of experience.

The foreign exchange component of production costs often presents a problem in a developing country where foreign exchange expenditures must receive express governmental approval. Usually, there is little difficulty with continuing and regular requirements for raw materials, operating supplies, etc., but there may be difficulty in obtaining foreign exchange for unpredictable requireinents such as the replacement of spare parts as soon as they are used. Failure to replace warehouse spare parts invites partial or complete loss of production at some future time, with attendant costs well in excess of the parts themselves.

### DISCUSSION OF SEVERAL BASIC INTERMEDIATES

Basic intermediates for the petrochemical industry may be defined as hydrocarbon compounds, recovered or produced from petroleum, which are primarily used as raw materials for conversion to marketable synthetic products such as plastics, fibres, rubber, detergents, solvents and pesticides. They may be classified into three types according to chemical structure, i.e., paraffins, olefins and aromatics.

The paraffins, which are the least reactive of the group, are methane, ethane, propane and butanes. These compounds occur in natural gas and in crude oil, and also appear as by-products of various petroleum processes such as cracking, reforming, etc.

The olefins, which are more reactive, include ethylene, propylene and butylenes. These materials do not occur naturally in petroleum but appear as by-products of petroleum processing, or can be produced at will from selected paraffin feedstocks. There are also two important related compounds of olefinic nature, acetylene and butadiene, which are made as principal products or by-products from selected feedstocks.

The aromatics, which are also highly resctive, are benzene, toluene and xylenes. Generally speaking, these compounds occur naturally in petroleum only to a limited extent, but certain types of crudes will yield aromatics more readily than others. These aromatics have traditionally been obtained as by-products of the coal tar industry but are now produced extensively from petroleum.

### interdependence of petroleum industry

Petroleum refineries have provided the base from which much of the petrochemical complexes have developed. Not only do the refineries provide raw materials such as hydrocarbon gases and liquids, but they also provide a convenient and economically attractive means of disposing of by-products as either saleable or refinery fuels.

In developed countries, the scale of the petroleum industry is so large and the range of products so diversified that the refinery can readily service an associated petrochemical complex. In developing countries, on the other hand, the refinery is likely to be less flexible with regard both to the provision of raw materials and to the absorption of by-products. For example, a refinery in a developing country may have one or more of the following characteristics:

1. The relatively low demand for gasolene and the lack of demand for premium grades of gasolene tesult in a refinery process scheme that will produce less light hydrocarbon gases (paraffins and olefins), which are desirable petrochemical feedstocks.

2. The market for liquefied petroleum gases (propane and butane) may consume most of the refinery production, leaving little or none as petrochemical raw materials.

3 The low demand for gasolene may impair the ability of the refinery to absorb and dispose of petrochemical by-products which are potential gasolene components.

4. The scale of the refinery may yield quantities of potentially valuable petrochemicals which are too small to justify economic recovery.

### Basic intermediates selected for discussion

It is neither feasible nor desirable to discuss each and every basic intermediate in this paper. We have selected for discussion acetylene, benzene, butadiene, and ethylene because these compounds are intermediates for nearly all of the plastics, fibres, rubbers and other products to be discussed in subsequent papers, and because the technical and  $\epsilon$  conomic factors involved in their production illustrate the general considerations previously discussed.

### Cost data

All production units have been converted to metric tons and all costs have been converted to United States dollars. Individual supporting costs have been stated separately when given in the original article.

### ACETYLENE

Acetylene manufacture from hydrocarbons has been increasing, but in the United States of America approximately 70 per cent of all acetylene is still produced from calcium carbide. Hydrocarbon-based acetylene is appreciably cheaper than carbide acetylene, but is more costly than ethylene. The latter statement is significant because, owing to recent advances in technology, ethylene is now an alternative raw material for nearly all the chief chemical derivatives of acetylene, except neoprene. These derivatives include vinyl chloride, acrylonitrile, acetaldehyde, acetic anhydride, and vinyl acetate.

On the other hand, the production of hydrocarbon acetylene can yield coproducts, such as hydrogen, and synthesis gas, which can be valuable in the manufacture of still other chemicals, such as methanol, ammonia, and their derivatives. There are certain derivatives, such as vinyl chloride, for which a dual feed of acetylene and ethylene offers processing advantages over a single feed.

Acetylene processes were extensively reviewed several years ago<sup>3</sup> based upor, conditions in the United States of America. It is worth noting that this article is a valuable example of explicit, complete delineation of the assumptions made and the resultant uncertainties in evaluating competitive processes. The principal results are summarized below.

The basic cost data used for the acetylene process comparison are reproduced below. They can be considered as representative of Gulf Coast (Houston Texas) costs, and are often used for general economic evaluation of petrochemical processes in the United States of America.

Natural gas         Ethane         Propane.         Bu 'ane         Naphiha         U tillities         Fuel         Power         Cooling water	\$0.20/million BTJ 0.007/pound 0.04/gallon 0.05/gallon 0.01/pound 0.20/million BTU 0.006/kWh 0.03/1,000 gallons 0.06/1,000 gallons 0.40/1,000 pounds	S0.0008/thermin 15.40/ton 20.80/ton 22.60/ton 22.04/ton 0.0008/thermin 0.0008/thermin 0.006/kWh 0.008/cu. metre 0.016/cu. metre 0.88/ton
Propane	0.04/gailon 0.05/gailon 0.01/pound 0.20/million BTU 0.006/kWh 0.03/1,000 gailons 0.06/1,000 gailons	20.80/ton 22.60/ton 22.04/ton 0.0008/thermic 0.006/kWh 0.008/cu: metre 0.016/cu. metre
Burane	0.03/gailon 0.01/pound 0.20/million BTU 0.006/kWh 0.03/1,000 gailons 0.06/1,000 gailons	22.60/ton 22.04/ton 0.0008/thermic 0.005/kWh 0.008/cu. metre 0.016/cu. metre
Naphiha	0.01/pound 0.20/million BTU 0.006/kWh 0.03/1,000 gallons 0.06/1,000 gallons	22.04/1on 0.0008/thermic 0.005/kWh 0.008/cu: metre 0.016/cu. metre
Utilities Fuel	0.20/million BTU 0.006/kWh 0.03/1,000 gallons 0.06/1,000 gallons	0.0008/thermic 0.006/kWh 0.008/cu. metre 0.016/cu. metre
Fuel	0.006/kWh 0.03/1,000 gallons 0.06/1,000 gallons	0.006/kWh 0.008/cu. metre 0.016/cu. metre
Power	0.006/kWh 0.03/1,000 gallons 0.06/1,000 gallons	0.006/kWh 0.008/cu. metre 0.016/cu. metre
	0.03/1,000 gallons 0.06/1,000 gallons	0.008/cu. metre 0.016/cu. metre
Cooling water	0.06/1,000 millons	0.016/cu. metre
COUNTRY MINING A 1 1 1 1 1		- ,
Process water	0.40/1,000 pounds	0.88/10n
Steam		
Labour		
Operating labour	3.20/hour	
Supervision	25 per cent of operat	ing labour
Maintenance.	4 per cont of investm	lent/year
Fixed charges		
Plani guneral expense	80 per cent of labour	and supervision con
Local taxes and insurance	2.5 per cent of investr	nent/year
Depreciation.	10 per cent of investi	men1/year
Interest	5 per cent of total ca	pital invested/year
Working capital and start-		
<b>нр селів</b> —	10 per cent of invest	ment
OSBL facilities.	30 per cent of (SBL	unit cost
Plant stream efficiency	90 per cent (330 day	s/year)
Purchased oxygen costs		
9,000 ton/year plant	\$7.70/ton	
22,500 ton/year plant	6.35/ton	
45,000 ton/year plant	4.55/ton	

### COMPARISON OF PROCESSES

Plant production rate (tons/year)	9,080	22,500	45,609
Process		daetaring ou I dellars/ten	
From carbide	36.69	36.00	35. <b>29</b>
From hydrocarbon gan			
Electric arc	24.00	21.80	17.30
Thermal cracking		13.60	11.60
Partial oxidation.		15.30	13.00
From naphths			
Thermal cracking	22.70	17.70	14.89
Partial exidation		21.89	18.20

<sup>\*</sup> W. E. Lobo, Chamical Engineering Progress, 57 (11):35-42 (November 1961).

Approximate investments used in the above calculations for the largest size plant (45,000 tons/year) are:

		IS <b>DL units</b> U <b>S duiturs</b>
Electric are		16,000,000
Thermal cracking.	· •	11-13,000,000
Partial oxidation .		9,750,000

The investments were scaled using a 0.6 exponent, as an approximation.

Since the morchant (i.e., pipeline) price for ethylene in the United States of America ranges between \$6.60 and 11.00/ton, the preference for ethylene can be readily understood. For a developing country, it seems likely that ethylene will also be preferable under most conditions.

### BUNZENE

**Bennene can be obtained from a petroleum refinery** by selective reforming of naphtha feedstocks and appropriate recovery, but the yield is low, in the order of 0.5-0.6 percent by weight for Middle-East crudes. Bennene is also formed as a by-product of ethylene manufacture from naphtha, and the yield can be as high as 25 per cent by weight on ethylene. Rough calculations show that a 50,000 ton/year ethylene plant could produce as much benzene as a 1,300,000 ton/year refinery (40,000 BPSD).

Bensone obtained as a by-product of ethylene manufacture has a lower cost benzene than from a refinery, the actual cost depending on the crude by-product value. Published data4 are available for a plant producing 60,000 tons/year of aromatics, of which 24,000 tons/year is benzene; they indicate a direct operating cost, on the basis of United States prices, of approximately \$15/ton of aromatics recovered, and an investment of approximately \$2,500,000. The direct operating cost does not include the cost of the crude aromatic gasoline feedstock, which would depend upon the local value of regular gasolene. The value of the beasene product would depend upon competitive sources within the country, if any, or the world market price for export benzene. In the United States of America, regular gasolone has a refinery value of \$35-40/ton, while benzone has a value of approximately 388/1on.

The other aromatics, toluene and xylene, may be used as such or they could be converted into additional beasene by hydrodealkylation processing. For a unit to convert 40,000 tons/year of toluene to beasene (20 per cent yield), the investment would be approximately \$1,250,000, and the direct operating cost approximately \$7.50 per ten of beasens.

Studies have shown that this scheme for benaue production from an othylene unit is more attractive then installing an aromatics unit in a refinery.

As a matter of interest, the stated cost basis for the bangane-from-othylone study is given below.

Raw materials	Excluded from direct operating costs
Utilities	
Fuel Power Cooling Water Steam	0.008/kWh 0.02/1,000 gallons
Labour	
Operating labour. Supervision	3.00/hour 20 per cent operating labour
Maintenance	3 per cent investment/year
Pixed charges	
Administrative and sales overhead. Depresistion	5 per cent of sales value of products 10 per cent investment/year 3 per cent investment/year
Working capital	Not included
OSBL facilities	Not included
Plant stream efficiency .	96 per cent (350 days/year)

It can be seen that some of the cost values differ from those set forth in the acetylene comparison, and furthermore that some costs are simply not included. These differences are not a question of "right" or "wrong"; they simply reflect different approaches to preliminary economic analysis, and underscore the general observations given previously in this paper.

### BUTADIENE

Butadiene, which is an important component for synthetic styrene-butadiene rubber (SBR), can be produced from a petroleum refinery butane-butylenes stream, or can be recovered as a by-product of ethylene manufacture from naphtha. There are also two older routes to butadiene, which are virtually obsolete for developed countries. The first uses acetylene as a raw material and the second uses formentation alcohol. Of these, the latter is used in two developing countries where fermentation alcohol is available at attractive prices.

The choice of feedstock for butadions for a developing country will be determined in part by the following considerations:

1. A large butane-butylenes stream is usually produced only by a large petroleum refinery with a catalytic cracking unit. Without going into details it may be stated that it is unlikely that a developing country would have this type of refinery because of the low domand for gasolene. The type of refinery most likely to be installed in a developing country would be directed towards the maximum production of heresine, direct and residual fuels, and therefore the availability of encess butanes is unlikely.

2. A significant yield of butadions can be obtained as a by-predect of othylane production from nephtha, but the scale of production is to be flairly large to justify a butadiene unit, since the yield of butadiene is approximately 10 per cent of the othylane product.

3. The east of the bundless produced from butter will very significantly depending on the value of the field;

<sup>&</sup>lt;sup>4</sup> W. M. Swassen and C. H. Wathins, Chandred Busineering Progress, 34 (12):55-89 (Becamber 1958).

the cost of butadiene from naphtha cracking will depend on whether the crude by-product is charged at fuel value or whether it bears some part of the naphtha cracker cost.

4. Under special circumstances, domestic fermentation alcohol may be desirable.

Indicative costs available<sup>4</sup> are given below for an annual capacity of 40,000 tons of butadiene from butanebutylenes feedstock.

Investment	\$19,000,000
Production cost	US \$iton
Raw material	31 (\$14/ton of butane feed)
Utilities, chemicals catalyst	71
Labour maintenance royalties	62
Overheads and depreciation .	105
	269

The effect of feedstock price is as follows.

	Peadstock price (US \$1000)										Jun	sreduct \$/sen)	****	
14													269	
28													294	
42				•									320	

The scaling factor for investment is approximately as follows (0.73 exponent):

Copecity (tota/your)									heventment (US\$)		
20,000											11 <b>,500,00</b> 0
40,000.											19 <b>,000</b> ,000

By-product butadions from cracking of naphtha to make ethylene requires only an extractior unit and therefore the production cost is 60-70 per cent of that given in the previous paragraph.

If a developing country had a choice between ethane or propane versus naphtha as a raw material for ethylene manufacture, its decision might be influenced by the simultaneous demand for butadiene. The higher cost of the naphtha-based ethylene unit might be offhet by the elimination of a costly butane-based butadiene unit. If the naphtha route were selected, the yield of butadiene can be maximized by appropriate selection of operating conditions. In Europe, by-product butadiene is now taking a considerable share of the market.

### ETHYLINE

### Current trends

In Burope and the United States of America, the cagnatties of new ethylene units are becoming larger and larger. In the past, plants with 50,000 tons/year especity

were considered to be large, however current European plants fall in the 70,000 to 200,000 tons range. In the United States current plant capacities are expanded to as high as 400,000 tons.

For most developing countries 45-50,000 tons/year would be a large plant. It would, perhaps take a regional group to justify an initial capacity of this level. A recent survey <sup>6</sup> supports this contention.

	Capacity (tons/year)					
Geographical region	Current	Planned additional capacity				
Latin America.	3,300	85,000				
Africa	None	Data not available				
Middle East	15,000	40,000				
Asia						
Japan	550.000	800,000				
Australia.	71	Some; exact date not avail able				
All others Sor	ne; data 101 available	In excess of 60,000				

Individual countries have production capacities, current or planned, as small as 7,000 tons/year. But more representativ of current planning is the range of 30,000 to 60,000 tons/year, with plants in the smaller or less developed European countries ranging up to 100,000 tons/year.

The most important raw material for the European and developing countries bas been naphtha, although there are some units based upon natural gas, coke oven gas or crude oil.

Japan provides a significant example of the current trends in ethylene production. All proposed petrochemical expansions are screened for approval by its trade ministry, MITI. A long-range demand-capacity survey carried out by MITI led to the following conclusions:<sup>7</sup>

- 1. Ethylene will maintain its position as the prime olefin (above acetylene and propylene).
- 2. Naphtha will remain the preferred starting material.
- 3. Ethylene demand will grow at a rate of approximately 50 per cent in 1965-1966, and approximately 20 per cent per year for the rest of the decade.
- 4. More than half the ethylene will be converted to polyethylene; the remainder, in decreasing order of amounts, will be converted to various plastics, fibres, paints, surfactants and rubbers.

The developing countries (excluding Japan) plan to use their ethylene capacity principally for polyethylene, with lesser amounts for polyvinyl styrene and acrylic derivatives. Only the countries with larger markets such as Japan, Mexico, and India are currently planning to convert ethylene to other derivatives with more sophisticated applications.

\* European Chemical News (June 19, 1964).

<sup>\*</sup> Burgean Chemical News, 20 June, 1942.

<sup>\*</sup> European Chemical News (September 11, 1964).

### Selection of unit capacity

A recent feature article<sup>8</sup> discusses the scaling factor for ethylene plants in some detail and states some interesting conclusions. For plants up to 200,000 tons/year capacity (the range considered in the article), the capital costs for the process unit will vary with the capacity according to a 0.7 exponent.

Using published investment and operating costs, the article considers the following problem and solutions.

				Ym					Predicied	Installed cap	acity tonsiyear
									ethylene demand (tons/year)	Case A	Can B
1		•							75,000	125,000	200,000
2	٠	•	•		•				100,000	125,000	200,000
3	•								125.000	125,000	200,000
4									150,000	2-125,000	200.000
5	•								125,000	2-125,000	200,000
6	·	·	·	•	•	•	•	•	200,000	2-125,000	200,000

Case A is based upon building one 125,000 tons/year plant initially and a duplicate plant three years later; case B is based upon building a single 200,000 tons/year plant initially. In neither case do the plants run at full capacity throughout the whole period.

The following table compares, for each year, the unit production costs expressed in United States dollars per ton of ethylene, and the cumulative cost of production (adding each year's cost to the previous year) expressed in millions of dollars.

The production costs include direct operating costs (naphtha charge stock, utilities, labour etc.) and 15 per cent/year of capital to cover depreciation and interest.

Year									ethylene)	Cumulative production costs (US millions of dollars)		
								Case 4	Case B	Case A	Case 3	
1.								63.40	68.60	4.76	5.13	
2.								<b>59</b> .70	63.20	10.72	11.41	
3.								57.40	60.00	17.9	18.9	
4.								63 50	57.60	27.4	27.6	
5.	•							61.50	<b>56.30</b>	38.1	37.4	
6.	•	•	•	•	•	•	•	59.80	55.00	50.0	48.3	

The table shows that when full production is reached in year 6, the single large plant (case B) shows an 8 per cent lower unit production cost, which is appreciable. Similarly, the cumulative production cost is lower, but only 3.4 per cent. In absolute dollars, the difference of 1.7 million dollars realized in six years is not large compared to the differential investment of more than SUS 6.75 million that must be put up initially to build the single large plant. It is likely that more refined calculations reflecting the time value of money would show that the risk in building the single large plant is not justified. For a developing country, which must allocase its capital or financing capabilities carefully, the justification would be even less.

\* European Chamical News (May 10, 1963).

On the other hand, the table does illustrate the benefits of building a large plant if it can run at full rate initially. For this modification of case B, the cumulative savings in production for a single plant over two half-size plants would be 8 per cent, or approximately \$5.6 million.

### Selection of naphtha feedstocks

It is worth noting that attractive price and delivery do not necessarily indicate the most favourable naphtha feed for an ethylene unit. The type of hydrocarbon compounds contained in the naphtha can affect significantly the unit raw material requirements, the yield and quality of by-products, and the investment and operating costs for the unit. Such effects can be calculated with reasonable confidence from the analysis of the naphtha and correlations which have been developed by specialists in the ethylene field.

Briefly, the principal types of hydrocarbons which are of importance are paraffins, naphthenes (non-aromatic ring compounds) and aromatics. Qualitatively, higher paraffin contents require less raw material, produce less by-products such as butylenes, butadiene and aromatic gasolene, and require less investment and operating costs, all expressed per unit of ethylene produced. Higher naphthene contents do just the opposite : they require more raw material, produce more by-products and require more investment and operating costs. Finally, higher aromatic contents produce results which lie between paraffins and naphthenes.

The specific economics obviously are subject to many variations, but the following generalizations summarize one published <sup>9</sup> investigation. For a 50,000-ton ethylene unit with typical United States Gulf Coast unit prices, and assuming all naphthas have the same unit cost:

(a) The increased feedstock cost for naphthenic naphtha is more than offset by the increased income from by-products;

(b) The increased direct and indirect operating costs are also offset by the increased income from by-products;

(c) Because the calculation is fairly sensitive to the value of the by-products, lower credits could reduce or even reverse the differential in favour of naphthenic naphthas;

(d) Furthermore, in a gasolene-consuming area, naphthenic naphthas often command a premium because of their higher octane number. Such a premium would also reduce the differential.

It follows from the above discussion that a prudent plant design would balance incremental investment against incremental flexibility to utilize naphthenic naphthas. It also follows that a prudent plant design would permit operation under various conditions that would modify the yield of by-products for a fixed feedstock. A considerable degree of flexibility can be provided in the basic plant which will be consistent with economic procurement of feedstocks over the life of the plant, and technological advances are currently being made in this area.

<sup>&</sup>lt;sup>4</sup> J. A. Knaus and J. L. Pation, *Chemical Engineering Progress*, 51 (8):57-61 (August 1961).

### Recent technological advances

Since naphtha is one of the most likely feedstocks for ethylene production in a developing country, recently reported advances in cracking furnace design<sup>10</sup> should be of considerable interest. The Lummus Company has developed and proven out a design that substantially improves the yields of desired products (ethylene, propylene and butadiene) with lower utility requirements and correspondingly lower investment. This fundamental type of improvement, which is applicable to all sizes of plants, is an outstanding illustration of improvements in technology that make it possible to reduce production costs for petrochemicals even though the basic materials and labour cost factors escalate.

### LATIN AMERICAN EXPERIENCE

### Mexico

Mexico provides an interesting example of a developing country favoured with good natural resources whose economy is "over the hump" and where new markets demand new industries, thereby raising the standard of living and creating or expanding existing markets. A recent article<sup>11</sup> points out that this market has made it possible to construct a reasonably sized installation which can operate at costs comparable to those in developed countries. A generalization is offered to the effect that if the Mexican market three years hence is as large as the smallest economically operating plant for that product in the United States of America, then the venture is sound for Mexico and can be a profitable investment.

With regard to modern techniques (the article goes on to say) a developing country is not burdened with obsolete equipment, and outdated ideas, but, on the other hand, cannot afford to be a "guinea pig" for techniques unproven in commercial practice.

Mexico is fortunate and far-sighted in having a large group of professional chemical engineers and skilled technicians, both of which are indispensable for the application of modern technology. These engineers and technicians made special note of the full use and understanding of automatic instrumentation, whose operation must be proper and reliable for the use of continuous processes.

Mexico is favoured with abundant supplies of crude oil and natural gas, and has installed extensive pipeline systems to distribute these vital raw materials to most parts of the country. It is able to import other basic materials needed at economic prices; this is an advantage, since Mexico can defer domestic production of some items until the demand justifies a reasonable size of plant. Mexico has substantially increased its electrical generation capacity, thus meeting a basic requirement of all process industry. Finally, enlightened over-all governmental planning and attractive climate for private investment have encouraged the rapid growth of a sound petrochemical industry.

<sup>11</sup> C. O. Baptista, Chemical Engineering Progress, 60:94-100 (June 1964).

For the basic intermediates which are of interest in this paper, Mexico has, or is planning to have, the following capacities:

Ethylene		35,000 tons/year (2 units of this size)
Aromatics		
Benzene		124,000 tons/year
Toluene		11,000 tons/year
Xylenes		14,000 tons initially,
•		45,000 tons ultimately
Propylene		Available from refinery operations

These basic intermediates will be used for many products, such as:

Ethylene	Acetaldehyde to acetic and to cellulose acetate fibre
	Polyethylene
	Ethylene dichloride to vinyl chloride
	Ethyl chloride to T.E.L.
Benzene	Cyclohexane to caprolactam to nylon 6
	Ethyl benzene to styrene to polystyrene
	Ethyl benzene to styrene to SBR rubber
	Cyclohexane for phenol
Propylene	Tetramer to dedecylbenzene (detergents)

Not all developing countries have assets equal to those of Mexico, but Mexico's use of its assets and its sound buildup of its petrochemical industry provide valuable guidelines to other developing countries.

### Argentina

Argentina provides another interesting example; it too has significant oil and gas resources, but its petrochemical development is less successful than Mexico's, having been beset by various economic and political handicaps. According to a recent article,<sup>18</sup> Argentina has too many small inefficient plants. Typical annual production capacities support this contention:

Aromatics							3,000 tons
Ethylenc .							13,000 tons

By contrast, similar plants under construction will have the following capacities:

Aromatics							26,000 tons
Ethylene .							
							12,000 tons
Butadiene							32,000 tons

A further handicap to Argentina's petrochemical development has been insufficient and expensive electric power supply. This has forced each plant to generate its own power, and has thus increased both the investment and the operating costs for each product.

<sup>18</sup> Chemical Week (September 12, 1964).

<sup>&</sup>lt;sup>13</sup> F. A. Firpo, *Chemical Engineering Progress*, 60:92-99 (May 1964).

### Brazil

The situation in Brazil is in some ways similar. Data given in a recent article <sup>18</sup> illustrate the problem of economic plant size versus demand even in a country as large as Brazil.

		C	Che	mi	cai					Est	ima	ted annual demand 1.965 tons
Ethylene												31.000
Propylene												3.000
Benzene												
Toluene												
Xylenes												
Acetylene								÷	÷	÷	÷	36.000
Butadiene	•									•		57,000

If all the ethylene were produced in a single plant, the level would still be on the lower side of economic plant capacity.

Another interesting factor in Brazil, which may well apply to other developing countries, is the availability of large quantities of domestic fermentation alcohol at a low price. As a result, both ethylene and butadiene are being, or will be, made from alcohol, which operations are not usually economic in large petrochemical industries in the United States of America and in Europe.

### Regional integration

The Latin America Free Trade Association (LAFTA) has addressed itself to the problem of the economic activity of the chemical industry in its member countries. As reported in a recent journal,<sup>14</sup> it believes that in the long run, integration of chemical industries on a regional scale represents the only solution that will satisfy all their economic and social objectives. Specifically, it concluded that for a wide variety of heavy and intermediate chemicals, the cost savings resulting from distributing industry throughout the over-all area on the basis of available resources and optimum-scale production, would be much larger than the increased transport costs. Furthermore, only in this way would prices and costs in the industry be comparable to those in the international markets.

Some of the major implications of such a programme at the plant level are:

1. Since some intermediates, such 2s ethylene, cannot be transported economically except by pipeline, the intermediate plant will probably be intimately associated with one or more derivative plants.

2. This will permit better use of by-products such as propylene, butadiene and aromatics, and perhaps more efficient use of waste heat.

3. Flexibility of the plant will be important because of the different technical and economic needs of the member owners.

### CONCLUSION

This paper has presented a fairly extensive discussion of the problems and costs associated with the transfer of advanced technology to developing countries, and has presented illustrative data for certain basic intermediate petrochemicals. It has also given some recommendations for the use of cost data which may be derived from the literature or which may be furnished to the developing countries by companies specializing in the petrochemical business.

We are aware that the application of the data and recommendations given herein still require the exercise of a considerable amount of judgement.

We can only say that it is not possible to be more specific in a general paper of thir. sort, and that we desired principally to point out some cost elements that might otherwise be overlooked.

In conclusion, we suggest that when the developing country has identified its scope requirements for both the ISBL and the OSBL facilities and can set them forth in an inquiry, then the prospective licensers and suppliers can supply data for a complete plant to meet those requirements, with sufficient accuracy for planning purposes. For final appropriations, time and cost required for definitive studies are nearly always indispensable and worth while.

<sup>&</sup>lt;sup>13</sup> R. Schellino and E. B. Leitao, Chemical Engineering Progress, 60 (4):85-86 (April 1964).

<sup>&</sup>lt;sup>14</sup> P. C. Reynoso, *Chemical Engineering Progress*, 60 (2):85-88 (February 1964).

TABLE 1. DIFFERENTIALS IN CAPITAL AND OPERATING COSTS OCCASIONED BY TRANSFER OF TECHNOLOGY TO DEVELOPING COUNTRIES

Basis: All differentials are applied to an "inside battery limits" process unit installed in the Houston area of the United States.

- 1. Differentials in capital cost for same scope of ISBL unit
  - A. Licences or know-how fees
  - B. Shipping costs of imported equipment, machinery and materials
    - 1. Export packing
    - 2. Lighterage and special loading charges
    - 3. Ocean freight and insurance
    - 4. Special unloading charges
    - 5. Import duties
    - 6. Warehousing
    - 7. Local freight and insurance
  - C. Construction costs
    - Importation of construction tools on rental or purchase basis, including spare parts for tools
    - 2. Importation of certain consumable construction materials
    - 3. Expatriate construction supervision, craft foremen and skilled labour
    - 4. Housing, commissary and similar facilities for expatriate personnel
    - 5. Unfavourable site conditions (limited access, inadequate roads, bridges, etc.)
    - 6. Longer completion time
      - (e) Procedural requirements for credit, payment, import clearance etc.
      - (b) Shipping schedules and consolidation
      - (c) Recruitment and training of local labour
      - (d) Sease nal construction limitations (monsoons)
      - (e) Inadequate priority within country for indigenous materials, freight cars, etc.
      - (f) Loss or damage during shipment
      - (g) Inadequate or insufficient tools and construction equipment
    - 7. Expatriate vendor specialists
    - 8. Licenser specialists
- II. Differentials in capital cost for increased scope of ISBL and OSBL unit

### A. Spare equipment

- 1. Installed spares
- 2. Warehouse spares
- 3. Standardization of equipment to reduce spares

### B. Incremental feed and product storage

- C. Maintonance facilities
  - 1. Shops (machine, electrical, pipe, instrument etc.)

- TABLE | (continued)
- Tools and mobile equipment
   Warehouses
- D. Marine facilities
- E. Housing and commissary
- F. Recruitment and training
  - 1. Expatriate personnel
  - 2. Indigenous personnel
- G. Commissioning and start-up
  - 1. Contractor specialists
  - 2. Vendor specialists
  - 3. Licenser specialists
- III. Differentials in production costs
  - A. Shipping costs for imported raw materials, catalysts, chemicals and operating supplies
    - 1. See item IB
  - **B.** Advisory services
    - Expatriate personnel skilled in production, engineering maintenance, marketing, etc.
  - C. Use of indigenous utilities and supplies
    - I. Direct cost premiums
    - 2. Quality or reliability deficiencies
  - D. Initial lower productivity of inexperienced personnel

### E. By-products

- 1. No local market
- 2. Quality improvement

### TABLE II. APPROXIMATE SCALING FACTORS FOR PETROCHEMICAL PLANTS

		elative capi	tal cost, po	r cent of ba	int .
Relative capacity		For var	ious expon	nna "n"	
Per cent of base	0.55	0. <b>60</b>	0.65	0.70	0.75
••••••••••	60.5	<b>5</b> 7.7	55.2	52.6	50.3
<b>10</b>	75.5	73.6	71.9	70.0	68.2
	88.5	\$7.3	86.5	85.4	84.3
	Base	Buse	Base	Base	Base
125	113	114.3	115.6	116.9	118.4
166	132.1	135.4	139	142.5	146.3
230	165.5	173.4	181.5	190.0	199.0

General formula :

Cost at desired capacity Cost at been capacity	(Desired capacity) *
Cost at been capacity	(Base capacity)

### 9. ECONOMICS OF OLEFIN AND DIOLEFIN PRODUCTION

### R. G. Craig, L. C. Doelp, A. K. Logwinuk, Houdry Process and Chemical Company, Division of Air Products & Chemicals, Inc., United States of America

As the developing countries seek to establish economic independence, it has been necessary to find and take advantage of available resources as building blocks toward the establishment of basic industry. The need for such basic industry is self-evident in that it brings about a spiralling economic revolution. Employment is increased, the standard of living is raised, the demand for trained personnel and technologists is fostered, and their availability nurtures the growth of new industry, which accelerates this spiral.

In general, the first responsibility of developing nations has been to increase the ability of their citizens to feed and clothe themselves. This has led to consideration of a basic fertilizer industry in order to provide higher yields of foods and textile fibres to fulfil the nation's internal needs. The export of some of the production surpluses has provided funds for the attainment of other basic requirements through imports.

In some areas where climatic conditions prohibit this approach and in others where the agricultural needs have been met, the search for basic manufacturing facilities has focused upon the petroleum industry and the gaseous hydrocarbons obtained during the production of petroleum. In some countries, fortunate to have crude petroleum production at present, there is a waste of natural resources through burning of excess gases. Countries not yet fortunate enough to have found petroleum are in search of it; however, even if immediate prospects for discovery are not too good, these countries have already established or are on the verge of establishing a petroleum refining industry. The point being made here is that gaseous hydrocarbons, whether occurring naturally or available as by-products of petroleum refining, are available in many countries but are not always utilized to the fullest economic extent. Among these gases are isobutane and normal butane. If these are converted to olefins or diolefins they become the basis of a new petrochemical industry, which in addition to supplying the internal needs of the developing country also offers products for export.

Isobutane and normal butane can be converted by dehydrogenation to isobutylene, butylenes, and butadiene. Butylenes can be used to produce polybutylene lubricants, alkylate, butyl rubber, alkyl aromatics, butyl alcohols, etc. Butadiene can be used to produce a variety of rubbers and other products having wide applications.

The obvious question is whether or not it is economically justifiable to install plants in developing nations which are small by comparison with those installed in highly industrialized countries. It is to this end that we direct this study and present the economics concerned with the installation and operation of a small Houdry Dehydrogenation Process plant for the production of mono-olefins and diolefins.

As an introduction to the economics it is desirable to describe this process and review the inherent chemistry.

### CHEMISTRY AND PROCESS DESCRIPTION

The Houdry Dehydrogenation Process is a commercially proven catalytic process for the conversion of  $C_8$  to  $C_8$ paraffins to corresponding mono-olefins and conjugated diolefins. The heart of the process is the catalytic reactor section containing a chromia-alumina catalyst which promotes the following chemical reactions (compound names and attendant heat effects are indicated):

Thus, all reactions are highly endothermic and produce an increased volume of total products. Furthermore, the thermodynamic equilibria are such that high temperatures and low pressures are desirable to maximize unsaturate productivity. Optimum reaction conditions usually fall within the following ranges:

	English units	Metric unus
Temperature	1,100-1, <b>250</b> °E	593-676°C.
Pressure, absolute Liquid hourly space	5-20 in. Hg	9.34-37.4 kg/m²
velocity	0.5 10 5.	0

Because of the thermodynamic limitations, the conversion per pass is not complete and unconverted reactants must be recycled through the reactor section.

Although the desired reactions (1-6) are quite selective, limited quantities of the following by-products are formed:

 $C_1$ - $C_8$  saturates and mono-olefins;

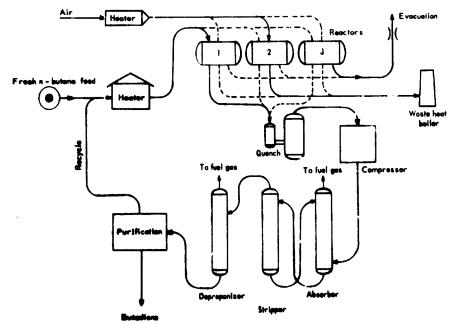
Coke;

Polymer.

Each of these products has value in its own right or with respect to the process. By gas plant separation, hydrogen is produced at 75-80 volume per cent purity and 75-250 psig, depending on the carbon number of the desired product. A 20,000 metric tons per year butadiene plant will produce about 2,250,000 standard cubic feet per day (SCFD) of hydrogen from n-butane fresh feed. It not used for its chemical value, the hydrogen is burned to supply process heat or generate steam and electrical energy. If the hydrogen is used as fuel  $C_1$  to  $C_2$  light hydrocarbons produced are also generally used for fuel. However, a fraction containing most of the Ca's is obtained and can be used for other purposes. Coke or heavy polymer is deposited on the catalyst and is burned off during the regeneration portion of the cyclic, fixed bad operation to provide essentially all of the heat of reaction. A small portion of the feed is converted to an aromatic oil, which is used in the process to quench the reactor effluent stream. The rate of production of quench oil is enough to overcome losses and degradation and keep the process self-sufficient.

The Houdry Dehydrogenation Process is capable of producing each of the products shown in reactions (1) to (6). Except for small differences in operating conditions and in the design of the product recovery section, the process components are the same for each operation.

Figure I shows a typical processing scheme for producing butadiene from normal butane. The same plant can be used for each of the other five reactions. N-butane fresh feed plus recycle n-butane and n-butylenes from the produce separation and purification section are heated to reaction temperature in a fired heater and flow to one of the fixed bed reactors. The reactors contain a shallow bed of pelleted chromia-alumina catalyst and granular inert material. The hydrocarbon feed enters at slightly below reaction temperature and the flow continues for a period of from 5 to 10 minutes. Since the net reaction is endothermic, the catalyst bed temperatures decrease during the on-stream period. A small amount of coke is deposited on the catalyst during the on-stream period. Reactor 1 of figure 1 is shown in the "on-stream" position. At the end of this period the reactor is purged with steam prior to the regeneration portion of the cycle. Air at about average reaction temperature is then admitted to the reactor to remove the coke from the catalyst. The exothermic combustion of the coke restores heat to the reactor bed equivalent to that removed during the on-stream period. The duration of the regeneration portion of the cycle is from 5 to 10 minutes. Reactor 2 of figure 1 is shown "on regeneration". Following regeneration, the reactor is purged and evacuated prior to repeat



Planes I. Hunter Datastranstan Press flow darram --- butalises from relations

ing the cycle. The total process time required for purging, evacuation and valve change is from 3 to 5 minutes, although more time may be allowed in the cycle. The total process cycle will vary from 15 to 30 minutes. Reactor 3 of figure 1 is shown "on purge" and evacuation.

The reactor effluent is taken immediately into a quench tower and cooled by direct contact with circulating quench oil. The effluent gas is compressed to 75-250 psig pressure and successively passes through an absorber, stripper and depropanizer. The depropanizer bottoms are fed to an extraction plant where 99 + per cent butadiene is separated from the unconverted butanes and butenes, which are returned to the reactor section. Butadiene separation and purification are accomplished using liquid-liquid extraction (cuprous ammonium acetate) or extractive distillations (acetonitrile, furfural, acetone).

The design and operation of the reactor section has a significant effect on process economics. From the standpoint of investment and utility costs it is desirable to have as high a conversion per pass to butadiene as possible, Since the butadiene formed is also subject to further reaction (degradation), increasing conversion (disappearance of fresh feed) is also associated with decreasing selectivity. Thus, as plant conversion increases, so does feed cost per pound of butadiene produced. Another factor influencing the operating conversion level is heat balance. Figure II shows a typical operating curve for butadiene production from n-butane fresh feed. The solid curve represents the relationship that is achieved between butadiene, wt. per cent total feed, versus coke wt. per cent total feed, as the level of conversion is increased. The dashed curve represents the heat balance line. At a given butadiene yield per pass (total feed), the dashed curve shows the coke required to produce an amount of heat (on combustion) equal to the net heat of reaction for the given butadiene yield. At the intersection of these two curves, point E, the net heat of reaction during the on-stream period is equal to the net heat of combustion of the coke deposited. Below this point (normal operating range), each cycle is deficient in heat by amount AB. This amount of heat must be supplied to the reactor by the sensible heat of the hydrocarbon and regeneration air streams or by other techniques which can be incorporated in the design. Above the point of intersection, excess heat equal to CD is produced on each cycle. Within limits this can be removed by the hydrocarbon and air stream. Traditionally, Houdry units have operated at levels substantially below point E of figure II. As a result of extensive commercial and laboratory testing, the invertion of a more rugged and selective catalyst, and the use of new analytical techniques to command instantaneous process control, operation near the heat balance point is now a commercial reality. The impact of this process modification on investments and operating costs is significant.

The achievement of the present-day version of the Houdry Dehydrogenation Process has been the natural result of continued engineering research and commercial experience. It is not uncommon to find plants operating with on stream factors greater than 95 per cent (over 98 per cent excluding turnaround). Some of the outstanding design features of the process are as follows:

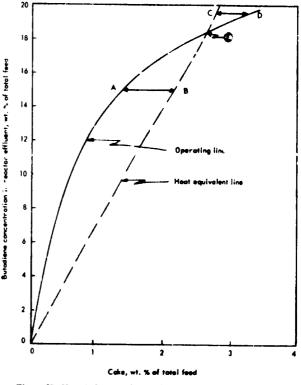


Figure II. Heat balance relationship production of butadiene from n-butane

(a) The refractory-lined, carbon steel reactors satisfactorily solve the problems which arise from high temperature operation in alternating oxidizing and reducing atmospheres. The expositre of even stabilized stainless steels to tnese conditions produces a catalytically active and undesirable surface. This condition is avoided in the Houdry design. Ceramic arches in the reactors support perforated tile, which in turn support the catalyst-inert mixture. The entire interior of the reactor and nozzles are lined with a special high quality refractory.

(b) The cycle timer automatically controls the dehydrogenation reactor section. The opening and closing of all the reactor valves required to carry the process through a complete operating cycle is controlled by electrical impulses from the timer. The timer also ensures that each operation is carried out safely. Prior to initiating each command it surveys the pressure in the reactor and the position of each pertinent valve to ensure proper positioning before allowing the next step to occur. Once it has initiated a given action, electrical wiring sufeguards prevent any other interfering action from taking place. Should the cycle timer fail to get a satisfactory report concerning reactor pressure or valve position prior to or following any action, it automatically stops, sounds an alarm, and locks into the existing mode of operation until the operating obstacle is removed.

(c) The cycle timer has at its command hydraulically or electrically operated valves which admit streams to and from the reactor. Valves as large as 42 inches in diameter are designed to fully open or close in a period TARLE I. HOUSEY DEPENDENTION PROCESS - TYPICAL MATERIAL BALANCES

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TARE 1 (contrast)

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### TABLE 2. HOUDRY DEHYDROGENATION PROCESS - TYPICAL MATERIAL BALANCES

Effect of conversion in butadiene production

Basis: 1,000 pounds fresh feed

Conversion		A	3 Itah			Me	4 deraie	
Component	Presh feed	Fuel	Buiadlene	Losses	Fresh food	Fuel	Butadiene	Loine
lydrogen		50		_	_	58		_
fethanc	—	68		-		29		
thylene.		37	_			15		
thane		42				17		
ropylene		74	-			31		
ropane.		33				13		
obutane	10				10	_		
obutylence		5				5		_
-Butylenes		21	3			25	3	
-Butane	990	16	_		990	18		
		5	529		_	6	644	
+, coke and loses		16	<del></del>	101		16		120
	1,000	367	532	101	1,000	233	647	120

of 21 seconds electrically or 5-6 seconds hydraulically. Each valve is designed to open and close without "slamming" but with sufficient force to ensure proper seating. The special valves for this service have been designed and built in the Federal Republic of Germany and in the United States of America.

(d) The dehydrogenation catalyst itself has undergone improvement over the years. The present catalyst possesses rugged physical properties, is very active and selective and is extremely stable to long exposures at high temperatures. This newly developed catalyst has been in commercial use for over two years, during whic'. over 1,100 tons of butadiene have been produced per ton of catalyst. Operation with this catalyst is continuing, so an ultimate catalyst life cannot yet be stated.

### PROCESS YIELDS

Yields experienced in application of the process to the production of various mono and diolefins are shown in tables 1 and 2. The product distributions shown in table 1 are based on high conversion operations at reduced selectivities to minimize plant investment and utility costs. This type of operation is applicable where feedstock costs are low, or where utility prices or capital costs are high. In all cases, the olefin is recovered as a separate product at the purity shows. Separation and purification plant losses — primarily  $C_0^+$  or  $C_0^+$  polymer---are included in the non-selective products.

Table 2 defines a different operation for butadiene production which can be attractive where feedstock is more costly. Operating costs will normally be high in this case when compared with the more severe operation of case 3 of table 1. This must be balanced by lower feedstock costs if the milder operation is to be justified.

### **PROCESS BCONOMICS**

Table 3 provides investment and operating costs data for the process when producing high purity propylene, isobutylene, normal butylenes, butadiene 1, 3, and isoprene. The basis for these economics is a single design for the catalytic, quench, compression and gas processing sections for all operations. Capacity is fixed at 20,000 STPY of butadiene from normal butane (case 3 of table 3). The productions shown for the other operations are those obtained in the same equipment when processing the same total feed quantity.

It is possible to produce isobutylene (case 2) and normal butylenes (case 5) in a somewhat less costly plant with some increase in feedstock cost. However, the flexibility of the process is shown most clearly if all products are produced in the same equipment exclusive of product purification. If capital costs are high the savings by a design specific to these products should be considered.

The product separation and purification sections of the plants described in table 3 are not identical for all the products. Thus, some differences in total plant investment and operating costs are shown. Actually, all the mono and diolefins can be separated reasonably well in the same extractive distillation equipment, but it has been commercial practice to separate propylene from propane by fractionation and to separate isobutylene from isobutane and other  $C_4$ 's by sulfuric acid extraction. The latter processes have been used in development of table 3 with extractive distillation used for all other separations.

Since substantial amounts of 50-150 psi steam are required in the product separation and purification sections of the plants, non-condensing steam turbine drivers have been used to the extent necessary to provide this steam. Motor drive has been used for all other power

		-	~	-	•	•	÷	~
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	· · · · · · · · · · · ·	\$5,000,000 2,000,000 100,000	25,500,000 2,200,000 100,000	\$\$,280,000 2,100,000 100,000	\$6,260,000 2,500,000 100,000	\$5,700,000 2,300,000 100,000	<b>\$</b> \$,230,000 2,100,000 100,000	\$5,200,000 2,100,100 100,000
	TOTAL	57,100,000	27,800,000	000'000/15	55,860,000	\$8,100,000	\$7,430,000	\$7,400,000
					<b>1 1 1</b>			
		ACCANA 2001.0 2000.0 2000.0 2000.0 2000.0 2000.0 2000.0 2000.0 2000.0 2000.0 2000.0 2000.0 2000.0 2000.0 2000.0 2000.0 2000.0 2000.0 2000.0 20	0.0165 0.1426 0.0147 0.0157	0.2605 0.2540 0.0125 0.00125	0.2260 0.0134 0.0005 0.0273	0.1575 0.0157 0.0005 0.0166	0.4300 0.2840 0.0125 0.0562	0.4480 0.4745 0.0240 0.0610
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	• • • •	<b>967</b> 1	1.430	1.890	1.475	1.440	1.488	2.007
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# TABLE 3. HOUDRY DERVEROGENATION PROCESS

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Production of high purity products — High conversion operations — Plant economics

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requirements. Naturally, driver selection is dependent on the price structure for each application. In many areas, partial or complete use of fired gas turbines to supply all power and regeneration air requirements proves economically attractive.

Table 3 shows clearly that production rate is dependent on the product desired and that manufacturing cost exclusive of feedstock is inversely related to the production rate.

The manufacturing costs including feedstock cost are shown in figure III as a function of feedstock cost. Normally, in the United States of America, saturated feedstocks cost between one and two cents per pound with the lower values applying in petroleum producing areas. In some areas of the world where flaring of light hydrocarbons is practiced, even lower feedstock values be used.

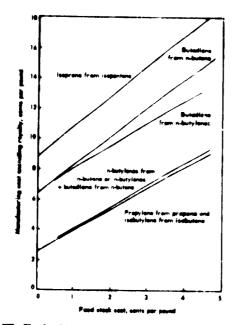
The yields shown in table 1 and the economic data presented in table 3 and figure III are based on high conversion operation. This is attractive whenever feedstock costs are low or whenever utility costs or capital costs are high. Where feedstocks are comparatively expensive, more efficient utilization of the feed (higher selectivity) may be desirable. Table 2 compares process

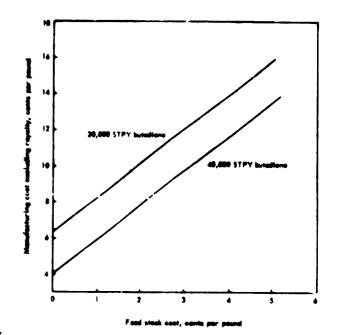
### TABLE 4. HOUDRY DESIYDROGENATION PROCESS. Effect of conversion and plant capacity in butadiene production --- plant economics

	4	11	12
Product (consulted butalline)	30,000 STPY	38,000 STPY	40,080 STPY
Conversion	<b>iliy</b> h	Moderate	
investment (USA Gulf Coast)			
Process units.	5 ≤,200,000 ∡,100,000 100,000	\$6,250,000 2,500,000 100,000	\$7,670,000 3,100,000 100,000
Тоты	\$7,400,000	<b>38,839,000</b>	\$10,870,000
L Jeilikinn		US cents per pound	
Puel 20 #/MM BTU Power 0.7 #/kWh	0.2005 0.2040 0.0125 0.0902	0.0095 0.3000 0.0242 0.0769	0.2605 0.2946 0.0125 0.0562
Sup-retal.	0.6132	1.1966	0.6132
Chemicala Solvent (32 ¢/lb.) Catalyst. Tert, Butyl. Cateshol (32.00/lb.) Other (520,000/yr.)*	0.0267 0.1232 0.0424 0.0550	0.0376 0.0839 0.0424 0.0550	0.0267 0.1232 0.0424 0.0500
SUB-TOTAL	0.2423	0.2139	0.242
Operating labour (see below).	0.7690 0.7390	0.76 <b>30</b> 9.8769	0.3025 0.5370
Bue-ref.M.	1.5040	1.6410	0.919
Plant overhead.	1.1475 0.1042 1.2275 1.5009	1.1475 0.2183 1.4680 1.5899	0.5737 0.1341 0.8975 0.7580
Bue total	4.0001	4.3238	2.399
Total (and, regnity and feedmont)	6.4187	7.2793	4.130
	1.890	1.991	1.899
	*		*

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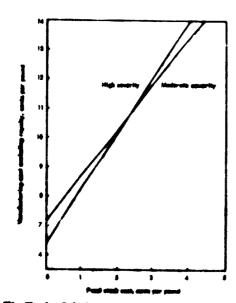
Pigure III. Mousky Dohydrogenation Process - affect of foodsook oost an manufacturing cost of high parity chemicals, high conversion

yields for high conversion production of butadiene from normal butane as used in tables 1 and 3 with lower conversion-higher selectivity operation. Table 4 provides economic data for these cases when producing 20,000 STPY of butadiene and figure IV compares manufacturing costs as a function of fundateck cost. These show that high severity operation is justified for fundateck ecets less than 2.4 costs per pound (for the assumed price structure). Above 2.4 costs per pound of fund, the cost of fund controls and the lower convenies.

Pignes V. Houdry Dubydrogenation Process — affect of foodstock over and plant capacity on butadiene manufacturing cost, high conversion

higher selectivity operation is justified although plant investment and utility and chemical costs are higher.

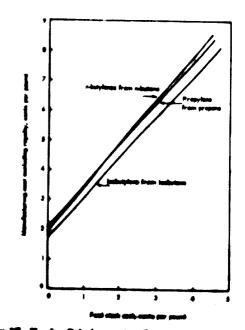
All the preceding economic data (and those in table 5 to be discussed later) are for plants capable of producing 20,000 STPY of butadiene or the equivalent of other oleftas. This appears, based on previous experience, to be an attractive espacity for developing nations. However



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Parts IV. Hendy Deladagenetis Press -- after of aprent sensity and federal and a branches -- after of aprent

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### TABLE 5. HOUDRY DEHYDROGENATION PROCESS FOR ALKYLATION PLANT PEEDSTOCK PRODUCTION

High conversion operations --- plant economics

	8	9	10
Product (contained basis)	49,600 STPY propylene from propane	55.200 STPY isobutylene from isobutane	48,630 STPY n-butylenes from n-butume
nveetment (USA Gulf Coast)			
Process units	\$4,180,000 1,600,000 100,000	\$3,500,000 1,600,000 100,000	\$3,560,000 1,700,000 100,000
TOTAL	\$5,880,000	\$5,200,000	\$5,360,000
Jtilities           Fuel, 20 #/MM BTU           Power, 0.7 #/kWh           Boiler fued water 30 #/M gal.           Make up water 10 #/M gal.	(0.0021) 0.1842 0.0058 0.0092	US cents per pound (0.0036) 0.1112 0.0052 0.0082	(0.0306) 0.1262 0.0059 0.0093
Sub-total	0.1971	0.1210	0.1108
Themicals			
Solvent 32 #/lb	0.1670	0.1158	0.1269
Tert. Butyl. Catechol \$2.00/lb	0.0202	0.0181	0.0255
Sub-total	0.1872	0.1339	0.1 <b>524</b>
Operating labour (see below)	0.2510 0.2330	0.2257 0.1848	0.2560 0.2163
Sub-total	6.4840	0.4105	0.4723
Plant overhead. Insurance and taxes (1 per cent of inv./yr.) Depreciation (15 yr. st. line).	0.3765 0.0582 0.3880 0.4040	0.3385 0.0461 0.3000 0.3622	6.3840 0.0541 0.3605 0.4110
SUB-TOTAL	1.2267	1.0548	1.2096
Total (end. royalty and feedsteck)	2.0950	1.7202	1.9451
Feed stock 1b/1b product.	1.395	1.365	1.485
Overeting men/shift *	7	8	8

· Includes general foreman for each shift.

States of

as would be expected, there are substantial economies to larger capacity plants. Table 4 provides economic data which show the advantages in manufacturing cost from installation of a normal butane to butadlene plant of 40,000 STPY capacity. Figure V compares manufacturing costs for the two plant capacities. Butadlene is 2.15 cents per pound less costly for the 40,000 STPY plant than for the 20,000 STPY plant. Similar effects also exist for olefin preducts other than butadlene.

If high purity chemicals are not desired, the dehydrogenation section effluent, which is high in momo-olefins, still has many uses. In the United States it has been used as alkylation plant feedstook for the production of aviation and utomobile fuel. Some chemical reactions can also utilize olefa and saturate mixtures. In this case ao separation or purification facilities are required. Table 5 presents economic data for the production of propyless, isobutylene and normal butylenes at about 50 per cent concentration diluted by their parent saturates. In the case of normal butylenes it is necessary to selectively hydrogenate the small amount of butadiene produced. Investment and utilities for this simple operation are included. Manufacturing cost of alkylation plant feedstooks are shown in figure VI.

If alkylation plant feedstocks are the desired objective, it is not even necessary to separate the feed into individual components; for example, isobutane and normal butane can be fed simultaneously. Conversion of isobutane to isobutylene can also be controlled to feed the alkylation section the proper isobutane to olefin ratio.

Isoamylenes, normal pentenes and piperylene are other  $C_s$  olefins which can be produced by the process should the need arise.

The Houdry Dehydrogenation Process offers an economically attractive means of producing mono and diolefins from the corresponding saturates. Flexibility of the process has been illustrated by production of various unsaturates in a unit designed for a specific diolefin. In a 20,000 STPY butadiene from n-butane dehydrogenation unit, a quantity of diolefin which may be internally absorbed by many developing countries, the production cost of butadiene exclusive of royalty and feedstock cost but on the basis of United States manpower and utility costs is 6.4 cents per pound. In the same dehydrogenation section, with some changes to the recovery section, isoprene can be produced for 8.8 cents per pound, isobutylene, propylene, or mixtures of n-butylene and butadiene for about 2.6 cents per pound.

Thus, dehydrogenation of saturated light hydrocarbons provides an economically broad base for a chemical industry. High purity chemical intermediates are readily produced for sale or for conversion to large volume bulk chemical products such as polypropylene or butyl,

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styrene-butadiene, polybutadiene or polyisoprene rubbers. Conservation of the valuable light hydrocarbon patural resource, which in some areas is now lost, also provides an incentive to the installation of dehydrogenation facilities.

### ECONOMICS OF OLEFIN AND DIOLEFIN PRODUCTION

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### **10. PRODUCTION OF ETHYLENIC HYDROCARBONS BY CYCLIC CRACKING**

A. Roche, Office national industriel de l'Asote and J. Lamarie, G.E.G.I. Company, France

The main processes for producing olefins can be classified in four different groups:

(a) Continuous cracking in tubes with external heating. Processes of this kind are the most commonly used and they lead to relatively high outputs in ethylene.

(b) Auto-thermic continuous or with partial-combustion cracking. These processes are used for acetylene production, ethylene being a by-product. They are interesting when acetylene production is the main problem.

(c) Continuous cracking on fluidized mass. These processes have a considerable flexibility and can use a great variety of feedstocks; however, they are all rather complex.

(d) Cyclic cracking. The catalytic and cyclic cracking processes for liquid and gaseous hydrocarbons have been used all over the world for producing synthesis gas, or rich gas. One of the better known among the cyclic processes, the "ONIA-GEGI" process has been the object of numerous experiments in the production of high ethylene and propylene content gas. The present report concerns this process.

### I. DESCRIPTION OF THE ONIA-GEGI PROCESS

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A plant using the ONIA-GEGI process includes essentially the following:

- One combustion chamber, in steel plate, internally lined with a refractory and insulating lining and supplied with a burner;
- One cracking chamber, in steel plate, also lined with a refractory and insulating lining and supplied with a contact-mass. This chamber is also supplied with a device for injection of the hydrocarbon to be cracked, mixed with steam;
- One waste-heat boiler to produce the necessary process steam by recuperation of sensible heats;

One scrubber-washer to cool the product gas;

One stack to send the heating waste gases to the atmosphere.

The operation is cyclic and comprises two main phases: heating and cracking; the cycle being automatically assured by a pre-set governor, stack and valves which are actuated, as desired, by hydraulic servo-motors or by electric jacks.

At the beginning of the heating phase, the feedstock and the combustion air are sent to the combustion

chamber burner. The waste gases produced go through the cracking chamber, then through the waste-heat boiler and are sent to the atmosphere. These waste gases are oxidized and the carbon deposited on the contactmass during the preceding phase is burnt while, at the same time, this mass is reheated to the required temperature for a new phase. At the end of the heating phase, a short steam purging phase takes place.

This is followed by the next phase, in which the hydrocarbon is intimately mixed with the steam and admitted in the eracking chamber. The hydrocarbon-steam mixture goes through this chamber where the cracking reaction takes place; the product gas leaves the reactor and after cooling in the waste-heat boiler and the scrubber-washer is sent towards the compressing station in order to separate the various constituents. Shortly before the end of the cracking period, a new steam purging phase takes place; then the cycle begins again.

The starting and shutting-off period of such a plant is very short. From the cold state, it is possible to begin gas producing after only eight to twelve hours preheating.

### 11. MAIN CHARACTERISTICS OF THE PROCESS

The reactor is particularly robust and simple; it permits very extensive cracking and, with liquid hydrocarbons, it is possible to obtain high ethylene efficiencies of about 35 per cent in weight of the feedstock used. The quantity of liquid gasolene collected, after cracking, is very small.

In view of the high ethylene efficiency and the low gasolene production, it may, in some cases, be considered economical to give up the sale of this gasolene, and to use it as fuel for heating.

The possibility of conducting the cracking in severe conditions allows the treatment of hydrocarbons the use of which was not formerly considered economical. It is then possible to crack propane as well as butane and light petrols, some heavier fractions and even some crude oils with ethylene efficiencies comparable with those obtained in using light paraffinic petrols.

As the variations in setting are extremely easy, the propylene/ethylene ratio can be varied very simply between 1/1 and 0.3/1 in weight.

When searching for a simultaneous yield of ethylene and propylene, the process gives the possibility to obtain a total olefins efficiency amounting to 45 per cent.

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FABLE 1. CRACKING OF LIGHT PETPOLS ON PILOT PLANT Per cent weight of products obtained of cracked, light petrol (before fractionation)

Light petrol s. gr. 0.668 Range : 44-108*C		Light petrol s. gr. 0.671 Range : 49-108°C		Light petrol s. gr. 0.733 Range : 32-198°C
Aromatic hydrocarbons	3.8	Aromatic hydrocarbons	0.6	Gasolene from Hassi R'Mel
Isoparaffinic hydrocarbons	24.6	Isoparaffinic hydrocarbons	32.0	
Paraffinic hydrocarbons	52.2	Paraffinic hydrocarbons	45.0	
Naphthenic hydrocarbons	- 19.4	Naphthenic hydrocarbons	22.4	
	· · · · · ·			
	100.0		100.0	

		Sulphur: ppn	•	_	Sulphur: 223	<b>pp</b> m	Sulphur: 13 ppm			
	Results fo	n three work	ing settings	Results fo	or three work	ing settings	Results f	or t <b>hree wor</b> k	ine settines	
C <sub>4</sub> H <sub>5</sub>	18.7	27.1	32.0	16.2	27.1	31.9	22.0	<b>26.2</b>	31.0	
	16.6	16.0	9.6	14.5	11.8	6.5	14.4	11.0	8.0	
Total ( $C_8H_4 + C_8H_6$ )	(35.3)	(43.1)	(41.6)	(30.7)	(38.9)	(38.4)	(36.4)	(37.2)	(39.0)	
H <sub>8</sub>	0.9	11.7	2.8	0.6	1.3	2.2	1.0	1.2	1.7	
	0.6	0.8	0.9	0.3	0.5	0.6	0.6	0.7	0.9	
CH <sub>4</sub>	9.7 3.6	15.7 4.2	21.1 4.4	9.0 3.3	17.5 3.5	23.5 3.5	10.9 2.4	13.7 3.6	18.7	
$\begin{array}{c} C_{a}H_{a} \\ \end{array} \\ \  \  \  \  \  \  \  \  \  \  \  \  \$	0.1	0.2	0.1	0.1	0.2	0.2	0.8	0.6	0.3	
	11.4	5.7	3.0	12.2	7.8	5.0	9.8	8.6	5.0	
TOTAL, gas other than ethylene and pro- pylene	(26.3)	(28.3)	(32.4)	(25.5)	(30.8)	(35.0)	(25.5)	(28.4)	(29.7)	
Condensate	32.4	21.5	17.0	39.2	23.3	15.5	36.0	29.6	16.4	
	6.0	7.1	9.0	4.4	7.0	11.0	2.1	4.8	14.9	
$C_3H_4$	1 <b>00</b> .0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100,0	
	1.12	1.68	3.33	1.12	2.3	4.9	1.53	2.38	3.9	

The ethane and propane content, in the product gas is very low; it corresponds approximately to half of that observed in the tubes cracking processes; it is therefore possible to simplify the separation plant. The process has a very high thermal efficiency and enough steam is produced to supply the plant's requirement.

### III. WORKING RESULTS ON THE USE OF LIGHT PETROLS

Numerous experiments have been made with light petrols, and table I indicates the results obtained with three of these; for each one, three columns of figures make it possible to show the variations in the results according to the adopted settings; the intermediate settings give intermediate results.

It may be observed that, from one petrol to another, the results given in this table do not necessarily correspond with identical settings of the apparatus. Moreover, under the name "condensates" is included all hydrocarbons collected in liquid form, after cracking; they contain in fact hydrocarbons having a carbon index equal to or higher than 5. Their composition is specified below. The line in the table named "carbon" includes the carbon found in the gas as  $CO_s$  and CO and the carbon deposited on the contact-mass during cracking. This carbon is burned during the heating periods with the excess air in the waste gases. The gases do not hold any free carbon.

The gas leaving the cracking plant contains, besides the components of table 1, some others such as  $CO_3$ , CO,  $O_3$ ,  $N_5$ , and table 2 gives, in weight and in volume, all the gases leaving the cracking unit for obtaining 50 t/day of ethylene starting from a petrol range of 40/110 with 50 mg/kg of sulphur.

The high olefins efficiencies obtained are slightly affected by variation in the feedstock composition used. Important variations of naphthenics contents in this feedstock have only a very slight effect on the ethylene of propylene yield; the aromatics hydrocarbons in the feedstock go through the reactor, with practically no change.

Table I, which is important in studying the market evolution of these two products in particular shows that:

The variations in setting make it possible to obtain a wide range in the ethylene-propylene ratio.

TABLE 2

	In weight (kg)	in volume (ml.
CO	4.040	2,050
$O_1$	161	113
CO	806	645
H	2,420	26,950
N	4,840	3,880
CH <sub>4</sub> · · · · · · · · · · · · · · · ·	32,300	45,100
$C_{\rm H}$	1,290	1,130
$C_{\mathbf{H}}$	50,000	39,700
	6,450	4,750
$C_{3}H_{4}$	14,500	7,800
$C_{\rm s}H_{\rm A}$	323	161
C <sub>1</sub> H <sub>1</sub>	2,420	969
$C_4H_6$	2,420	1.000
	121,970	134,248
Condensate:		
Petroli	26,130	
<b>Oil</b>	1,370	
Impurities in gr/Nm <sub>8</sub> :		
Naphthalene	0.6	
Tar	0.02	
SH,	0.025	
Organic sulphur.	0.025	

The weight of ethylene and propylene obtained, is so much more important than the settings for ethylene production.

- The weight of condensate decreases with the increase of ethylene yield, but, even in the case of a setting for a maximum of ethylene, the condensate quantity is sufficient to permit the heating, if desired.
- The light petrol sulphur content does not seem to influence the cracking during the cracking phase. This sulphur is hydrogenized to  $H_2S$ , which fixes itself partially on the contact-mass from which it is removed under the form of SO<sub>2</sub> during the heating. The sulphur found in the gas is in small quantity and under the form of  $H_2S$ .

It should be added that:

- The steam produced by the recuperation of the wastegases and the sensible leats furnishes the plant's steam requirement.
- The heating can be obtained by a hydrocarbon, the condensates, residuary gases, etc. Several possibilities can even be provided simultaneously if desired.

### Butadiene production

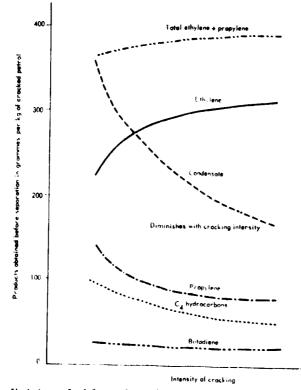
The results of systematical tests inade on a fixed petrol to verify the butadiene production are shown by the curves in the figure. These tests show that, if the total amount of carbides in  $C_4$  decreases much with the increase of ethylene proportion, whereas, the butadiene yield is practically constant. It is probable that, in some cases, and for a maximum ethylene yield, the hydrocarbons in  $C_4$  will be only in the form of butadiene.

### Condensates

Table 3 below specifies, for two fixed petrols, the condensates composition. This last one varies according

light petrol : s. gr. 0.657 — Range 3	0-405 ℃			Light petrol s. gr. : 0.733 Range 32-198°C								
		Per cent				Per	cent					
Condensate				Condensate								
Feedstock	31.2	25.4	155	Feedstock	38.7	24	18	16				
Octane number	<b>84</b> .7	92.0	<b>97</b> .1	Octane number	89.9	96.1	100.4					
Specific gravity at 15°C	0.672	0.707	0.843	Specific gravity at 20°C	0.732	0.797	0.839	0.882				
Anilin point	44	28	7	Per cent of condensate hydrocarbons :								
Per cent of condensate hydro- carbons :				Aromatic	39.2	66.7	84.6	<b>98</b> .6				
Aromatic	15.2	31.0	60.5	Olefinic	16.8	6.9	5.1	1.4				
<b>Oiefinic</b>	7.5	8.4	7.0	Paraffinic	43.9	26.4	10.7					
Parafinic	77.3	60.6	32.5	Per cent of aromatics								
				Benzene	51.0	60.5	64.5	69.5				
				Toluene	27.7	28.0	25.2	21.2				
				Xylenc.	21.3	11.5	10.3	9.3				

### TABLE 3



Variations of olefins and gasolene amounts following cracking in comparison with this cracking intensity (light petrol, d:0,733 fraction 32/198°C)

to the petrols used and for the same petrol, according to the ratio "condensate feedstock" the condensatecontent in aromatics is so much the higher than the ethylene proportion is itself the higher in the gas made.

### IV. USE OF OTHER FEEDSTOCKS

With the ONIA-GEGI process it is possible to use a wide range of feedstocks, from ethane to some crude oils. Table 5 below, shows the results obtained with some commercial propane, for two different working settings.

### V. FRACTIONATION

The ethylene, the propylene, the butadiene and the other fractions can be separated from the cracked gas by the classical processes. The relatively weak concentrations in ethane and propane make it possible to reduce the deethanization and the depropanization price.

### VI. CONCLUSION

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The ONIA-GEGI process, formerly set up for the production of town gas, synthesis gas, rich gas, etc.,

offers the following advantages if applied to ethylene production:

- It allows very intense cracking.
- In the tubular type reactors, the carbon deposits limit the ethylene yield. The ONIA-GEGI process makes it possible to obtain up to 35 per cent in weight of the feedstock.
- The gasolene production is considerably reduced, thereby reducing the ethylene cost. This gasolene can, in some cases, be economically used for the heating of the apparatus.
- The possibility of working in intense cracking conditions makes it possible to use feedstocks which, previously were not economical. The most difficult of these feedstocks (oils, fractions containing big quantities of isomeric paraffins) to crack by conventional methods give nearly the same yields of ethylene as the straight-run paraffinic naphthas ordinarily used.
- In the production of ethylenc and propylene, the process can lead to total olefins yields of as much as 45 per cent in weight of the feedstock. It is easy to vary the propylene-ethylene ratio.
- The amount of ethane and propane produced are small, which makes it possible to reduce substantially the separation equipment.
- The operation of the production apparatus is flexible and easy.

TABLE 4

PER CENT WEIGHT OF PRODUCTS OBTAINED OF CRACKED PROPANE

						Co					•						
	C <sub>s</sub> H <sub>s</sub>	• •															80.4
	C <sub>I</sub> H <sub>I</sub>												÷		÷	÷	19.4
	N <sub>2</sub> .	• •	•	·	•	•	•	•	•		•	•	•	•	•	•	0.2
																	100.0
						····•						Fo	, I	wø	W	wkk	g seilings
											:	29	5				36.8
C,H,	• •	• •	•	•	•	•••	•	•	•			14	0.				9.3
	TOTAL	. <b>C</b> <sub>1</sub> I	-1 <sub>4</sub> -	╉	C,	H,				-	 (	43	.0)	)			(46.1)
H				•	•							2.	8				4.4
C <sub>1</sub> H <sub>4</sub> .	• • •	•••	•	•	•	• •	•	•	•			0.	8				1.2
СН4.	• • •	•••	•	•	•		•	•	•		1	17.	8				27.6
jH.	• • •	• •	•	•	•	. ,	•	•	•			9.	2				4.9
C <sub>1</sub> H <sub>4</sub>	•••	•••	·	•	•	•••	•	•	•	-	2	4.	7				11.0
										-	(	55	3)				(49.1)
Carbo	_											1.					4.8

### 11. TECHNICAL AND ECONOMIC CHANGES IN ETHYLENE MANUFACTURE

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### INTRODUCTION

The amazing increase in world production and consumption of the leading plastics, such as polyethylene, polyvinylchloride and polystyrene, would not have been possible without the development of successful methods of producing their most important base material, the monomer ethylene, in large industrial operations at low cost.

It is interesting to note that the development of ethylene to the position of the organic chemical industry's first base material took place in a period of barely fifty years.

Even before its use gained industrial importance, ethylene was known to be present in the gaseous byproducts from industrial chemical processes based on the high temperature treatment of solid fuels such as lignite and coal. In coke-oven gas, for instance, ethylene occurs in a concentration of a few per cent. The economic use of this ethylene became possible only after the invention of the ammonia synthesis shortly before the First World War. To satisfy the increasing demand for hydrogen, low temperature fractionation plants were built to purify the hydrogen present in large concentrations in coke-oven gas. This operation yielded by-product hydrocarbon gases in which the ethylene appeared in concentrations up to 30 vol. per cent, which made its recovery economically possible.

In later years, refinery gases became available from thermal or catalytic cracking operations of oil fractions. These gases contained ethylene in concentrations which under the conditions then obtained, made possible its economic recovery and use.

When subsequently, the consumption of ethylene based products began to grow at an accelerated pace, the availability of ethylene from the sources mentioned fell short of requirements. The scattered nature of refinery operations and the lack of economic means of transporting ethylene aggravated the problem.

This situation stimulated research for industrial processes to convert organic material into ethylene.

After temporary and local success of the dehydration of ethanol, which was carried out particularly in the United States of America and the hydrogenation of acetylene, which was featured in Germany, the economic conditions ultimately promoted the development of thermal conversion processes using hydrocarbons from petroleum as feedstock. This development soon rendered the former processes obsolete.

From a yield stat.dpoint, the most obvious raw materials for the production of ethylene are ethane and propane and these were the hydrocarbons employed in the first ethylene manufacturing plants of this type built in the United States of America. However, ethane and to some degree also propane share the disadvantage of ethylene's high costs for transportation over long distances. Furthermore, ethane is generally available in natural gases in relatively low concentrations only and the separation of the ethane from the gas stream adds considerably to the total manufacturing costs. Investigations conducted on the thermal conversion of other, heavier, hydrocarbons revealed that economically attractive yields of ethylene could be achieved, provided that at least a part of the by-products could find a useful application.

The rapid development of the world demand for middle distillates and residual fuel oils derived from crude oil, in comparison with the growth rate of light distillate consumption, caused the latter to be available in surplus quantities. This fortuitous circumstance promoted the increasing use of ethylene manufacturing processes based on naphtha fractions, which are fractions having a boiling range between 30-40°C and 180-200°C.

Since this paper is based very largely on experience gained in western Europe, it will deal mainly with ethylene manufacture from light naphtha.

To provide a general technical background for the arguments to follow, a description is given, in section I, of a typical modern ethylene plant.

In sections II and III an analysis is given of the economic and technical changes that have been influencing the economics of ethylene manufacture in the last decade and which have jointly led to such a spectacular reduction in the cost of this important chemical building block. These cost aspects are discussed in section IV.

To gain some insight into the feasibility of manufacturing ethylene-based chemicals for remote markets, the movement of transportation costs for the main ethylene derivatives over the last ten years is discussed in section V.

Finally, some conclusions from this study are drawn in section VI.

I. DESCRIPTION OF A TYPICAL MODERN ETHYLENE PLANT

A number of processes for the pyrolysis of several types of hydrocarbons and for the gas separation and ethylene purification have been proposed and have, in part, found practical application. For the pyrolysis, the normal tubular furnace has found the most wide-spread application and as far as gas separation techniques are concerned, economic circumstances in most parts of the world seem to favour lowtemperature fractionation for all separations between the main fractions.

In order to facilitate further discussion on technological and economic aspects, the process route of a typical modern ethylene plant will be followed, combining pyrolysis and gas separation techniques as mentioned above, using the simplified flow scheme shown in figure I. The hydrocarbon feed, for instance a light straight-run gasoline fraction (light naphtha or tops) enters the convection section of the furnace or furnaces (1) after some preheating by a hot process stream. At a suitable point in the convection section, dilution steam is added in a weight ratio to the hydrocarbon feed which may vary from 0.5 to 1.

Dilution steam is added for a number of reasons. First, it lowers the partial pressure, thereby promoting the production of olefins and retarding undesired condensation reactions. Secondly, since team takes part in the reaction to a negligible extent only, the heat requirements per unit volume to sustain the endothermic reaction decrease upon steam dilution and a steeper temperature gradient along the tube coil can be achieved for a given heat input.

After leaving the convection section, the mixture of vaporized naphtha and steam is introduced into the radiant section of the furnace, where the pyrolysis, which comprises a complex sequence of predominantly endothermic reaction steps, takes place. The exit temperature of the furnace may vary from 750 to 830°C depending on the type of feedstock and cracking severity desired. Heat is supplied by burning gas or light distillate fuels. After passing through the convection section, the hot flue gases are utilized for steam superheating and boiler feed water preheating. The hot product gas, after leaving the furnaces, has to be cooled down very rapidly in order to arrest further reactions in the gas mixture, which would reduce the ethylene yield and result in tarry polymer and coke formation. This r. pid cooling is accomplished in the so-called quench exchangers (2) by direct highpressure steam generation. The steam production of these exchangers normally exceeds the dilution steam requirements. The pressure difference between the steam from the quench exchangers (up to and above 80 atm.) and the dilution steam injection point is utilized to drive a back-pressure steam turbine in the gas compression section.

The quenched pyrolysis gas is further cooled in a tar-wash tower (3). In the bottom part of this tower a circulation of polymer oil is maintained. The circulating oil is cooled by the fresh naphtha feed and by cooling water in a trim cooler. In the top part, gasoline reflux is given to achieve a fractionating effect for gasoline endpoint control. The overhead gases are passed through a water cooler and cooled down to ambient temperature.

The major part of the process steam and a substantial part of the gasoline fraction are condensed at this point. The gasoline condensate is used as reflux in the tarwash tower as mentioned above and the surplus is sent to a gasoline rerun tower (not shown).

The cooled pyrolysis gas is now fed to the feed gas compression section (4). In this compression section the gases are compressed in four stages, with intercooling between stages, to the desired end pressure of 32 to 35 atm. During compression and cooling substantially all the water contained in the feed gas is condensed along with the remainder of the gasoline fraction, a major part of

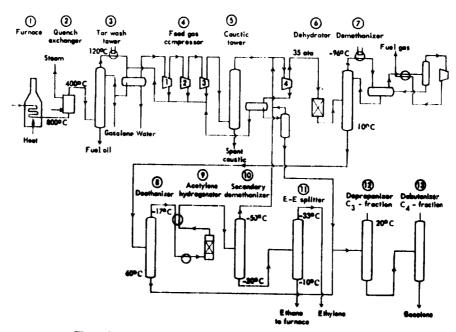


Figure L. Ribylene manufacturing unit, pyrolysis and gas separation

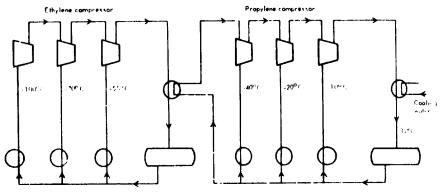


Figure II. Ethylene manufecturing unit, refrigeration

the C<sub>4</sub>-fraction and a part of the propylene/propane. After the third stage, carbon dioxide and hydrogen sulphide are removed in a two-stage caustic scrubbing tower (5) with a weak caustic soda solution. These components are unwanted in the hydrocarbon products and would, moreover, have various ill effects in the following processing steps, such as freezing in the low-temperature separation section and catalyst poisoning in acetylene hydrogenation.

The compressed feed gas is subsequently dried in a twc-stage dehydrator (6) filled with activated alumina or molecular sieves, to a residual water content of a few parts per million, in view of the low tolerance limits for the low-temperature distillation section.

After the dehydration stage the cold section of the gas separation follows, in which temperatures below ambient level down to  $-100^{\circ}$ C are encountered. Cooling is provided with refrigerant compression cycles, the principle of which is shown in figure 11. In the first cycle propylene evaporates, picking up heat at several desired temperature levels and is ultimately compressed to such a pressure that it can be condensed with available cooling water. In the second cycle, compressed ethylene is condensed against evaporating low-pressure propylene. The lowest temperature which can be reached with evaporating ethylene is about  $-100^{\circ}$ C. Sometimes a third compression cycle with methane refrigerant is provided for, but this is not generally required.

The purified and dried pyrolysis gas is chilled with cold process streams and with refrigerant in several stages of the propylene and ethylene refrigerant cycles before it enters the demethanizer column (7). The top gas of the demethanizer is cooled down with refrigerant in the lowest stage of the ethylene refrigerant cycle in order to condense the required reflux quantity.

In order to achieve a further drop in the ethylene content of the overhead gas from the demethanizer a gas expansion turbine may be installed with which a further temperature drop and an additional liquefaction can be obtained. The net top product of the demethanizer then consists of a mixture of hydrogen and methane with some traces of carbon monoxide and nitrogen, apart from small remaining quantities of ethylene, acetylene and ethane. The relatively low temperature of the de-

nicthanizer bottoms allows the reboiler to be heated by condensing a part of the propylene refrigerant at a lower pressure than the required normal end pressure of the propylene compressor for condensation against water, thereby saving incremental horsepower.

The demethanizer bottoms are flashed into the deethanizer (8). Here the  $C_s$ 's are separated from the  $C_s$ 's. The reflux is condensed with an intermediate level of propylene refrigerant as coolant.

The overhead of the de-ethanizer is heated up by heat exchange with process streams which need cooling and steam heating to the required temperature for acetylene removal by hydrogenation in the reaction section (9).

For this purpose hydrogen has to be added either from an extraneous source or prepared from the tail gas in a special low-temperature flash separation section.

The acetylene hydrogenation is carried out over a catalyst which is normally a noble metal (palladium) on an alumina support. After hydrogenation, traces of excess hydrogen and any inerts, introduced with the hydrogen, are removed in a secondary demethanizer (10).

The top gas of this column, in itself only a small stream but containing a high percentage of ethylene, is recycled to the section of the fourth stage of the feed gas compressor (4). The bottom product of column (10) is now directed to the ethylene/ethane splitter, column (11). The boiling point difference between ethane and ethylene is rather small, so that, depending on the required purity, a large number of trays (up to 90 or 100) and a high reflux ratio (up to 5 to 1) is required. The column operates at a pressure which allows condensation with the lowest propylene refrigerant level.

A normal specification for polymerization-grade ethylene is shown in table 1.

The bottom fraction of the column (11) is evaporated by exchange against the feed of the demethanizer and is subsequently recycled to a separate ethane pyrolysis furnace, which is not shown.

The bottom product of column (8) is transferred to column (12), the depropanizer, where a propylene/propane fraction containing up to 95 per cent of propylene is taken overhead. Modern plants frequently include hydrogenation facilities to remove methyl acetylene and TABLE 1. SPECIFICATION FOR POLYMERIZATION GRADE ETHYLENE

Total puri	ly.								Over 99.9 per cent vol.
									Below 500 ppm
									Below 500 ppra
									Below 10 ppm
									Below 10 ppm
									Below 5 ppm
Sulphur co	om	po	ne	ni	S.				Below 4 ppm
									Below 100 ppm

propadiene from the propylene fraction, which are objectionable constituents for many processes in which propylene is used as the base material.

The bottom fraction from the depropanizer is fed to the debutanizer (column 13), which controls the  $C_4$ -content of the gasoline.

The gasoline product from the debutanizer may be rerun in a separate column, which is necessary if, for example, flushing oil is used in the feed gas compressors to prevent polymer deposits.

A typical composition of the butane fraction is given in table 2.

TABLE 2. TYPICAL COMPOSITION OF C4-FRACTION IN NAPHTHA PYROLYSIS

Isobutane. Isobutene.									1 per cent wt 35 per cent wt
N-buiene-1						•			16 per cent wt
Trans-n-bu Cis-n-buten	te: IC-	ne 2	-2	}				•	6 per cent wt
Butadiene	1,3	١.							28 per cent wt

Typical properties of the gasolene may be as indicated in table 3 below.

TABLE 3. TYPICAL PROPERTIES OF PYROLYSIS GASOLINE

Research	ı C	)N	•	cł	cai	r.	•	•		•	97
Motor C	)N		ck	DA.	۲.						86
Maleic s	nt	iyo	İri	de	V	h	ie.				145
Benache											23 per cent wi
Xylencs											6 per cent wi
Toluene											12 per cent wi
Other ar	OE		tic	8.							4 per cent wi

Octage-symbol.

The composition of both the  $C_4$ -fraction and th<sup>e</sup> gasoline fraction may vary greatly, however, accordin<sup>g</sup> to the type of feedstock and the severity of pyrolysi applied.

Some typical yield patterns from pyrolysis furnaces for various feedstocks are shown in table 4. It should be noted that the yield pattern for light naphtha represents an average severity.

#### TABLE 4. YIELD STRUCTURES FOR THE PYROLYSIS OF VARIOUS FEEDSTOCKS IN A SINGLE PASS

Feed	Ethane	Propane	Light naphtha	Gas.ell 1.gr. 0.8	
Furnace exil temperature Steam to hydrocarbon	825°C	800•C	760°C	745•C	
ratio	0.33	0.40	0.5	0.7	
Composition, per cent wt					
Hydrogen	3.0	0.9	0.9	0.8	
Methane	7.4	26.4	12.7	11.7	
Acetylene	0.6	0.2	0.2	0.2	
Ethylene	42.9	32.2	24.0	22.4	
Elhane	37.3	6.8	5.0	2.1	
Propylenc.	2.3	11.9	19.7	11.7	
Propane.	0.9	10.8	0.5	0.6	
C <sub>6</sub> -fraction	1.1 )	10.8 *	9.8	10.1	
C <sub>a</sub> 's and higher	4.5	10.8 *	27.2	40.4	

\* Average molecular weight == \$0.

#### II. ECONOMIC FACTORS IN THE ETHYLENE FIELD

There is no doubt that the most important single factor which has influenced the field of ethylene based chemical products has been the very rapid growth of demand for these chemicals.

This development --- like so many others --- began earlier in the United States of America than in Europe. The enormous increase in car production in the United States of America since about 1930 pushed up the demand for ethylene oxide (for glycol) and ethylchloride (for TEL). The industrial consumption of ethanol also increased rapidly and for several years, ethylene oxide and ethanol were competing for first place among ethylene derivatives. Further demand for ethylene arose from the rapid development of the synthetic rubber industry during the Second World War and, in particular, from the spectacular growth of ethylene based plastics thereafter. The fastest grower among these plastics is, of course, polyethylene but the continuous, though more gradual, increase in demand for the older plastics polystyrene and polyvinylchloride has also contributed to the growing demand for ethylene.

The result has been that ethylene has developed from a by-product of coke-oven and refinery operations to the largest base material for the organic chemical industry. This point is aptly illustrated by the following figures. TABLE 5. BASE HYDROCARBONS CONSUMED IN CHEMICALS MANUFACTURE IN THE UNITED STATES OF AMERICA, 1961

																			Tons
																			380,000
Acetylene. Ethylene																			2,700,000
Propylene																			1,1 <b>70,</b> 000
Polylenes.	•	•	•	•	•	·	·	·	•	•	·	·	•	·	·	·	•	·	1,440,000

The growth of ethylene production in the United States of America since 1954, when consumption had already by far surpassed the million tons per year level, is shown in:

 TABLE 6. Estimated United States PRODUCTION OF ETHYLENE

 (Thousands of ions/annum)

1954	1957	1960	1963	(1966)
1,380	1,790	2,470	3,150	(3,950)

The average annual growth rate of United States ethylene production was 9.25 per cent for the period from 1957 to 1963.

In western Europe, ethylene made its appearance as a petroleum chemical product in the United Kingdom after the Second World War. After a fairly slow start, growth has been extremely rapid as is evidenced by the figures given in table 7.

For the period 1957/63 these figures correspond to an average growth rate of 30 per cent per annum. This trend is expected to continue, although at a slower rate (some 16 per cent) to reach a production level of some 2,800,000 tons by 1968.

Another interesting feature in this table is the overtaking of EFTA by the EEC in ethylene output in the later years. This is caused by the early start in large-scale ethylene consumption in the United Kingdom — polyethylene by Imperial Chemical Industries — so that in 1955 still over half of western Europe's ethylene was

TABLE 7. ESTIMATES OF WINTERN EUROPEAN PRODUCTION OF STHYLENS

(Thousands of ions/annum)

	1954	1997	1960	1963	( 1986)
EFTA	90	155	270	455	
EBC	50	115	405	835	
TOTAL WEIGHT	140	270	675	1,290	(2,100)

produced in that country. The gradual change-over in the Federal Republic of Germany from its largely acetylene (from coal) based chemical industry to the increasing utilization of ethylene was also an important factor in this shift.

It is clear that the increased demand for ethylene based products enabled the industry to build increasingly large plants to manufacture ethylene and ethylene derivatives in which production costs were reduced. The resultant lower selling prices for ethylene based chemicals, in turn, further increased the demand.

Whereas an ethylene plant producing 20,000 t.p.a. was considered large in 1955, units of 100,000 t.p.a. and over are now being constructed in many places. Also several units in excess of 200,000 t.p.a. are in operation or under construction.

Apart from the direct influence, however, of the scale of production on manufacturing cost — and hence on selling prices — the growing demand for ethylene, combined with the competitive spirit, has provided a powerful stimulus for the realization of technical improvements in the manufacturing process, which in turn have given rise to further cost reductions.

The savings that have been realized in ethylene manufacture in the last decade are due to the combined influence of these economic and technical factors. Before reviewing these cost reductions in some detail, it will be necessary to review the technical changes and improvements that have occurred.

### III. TECHNICAL IMPROVEMENTS IN ETHYLENE MANUFACTURE

In discussing this subject it will be convenient to deal separately with the developments in pyrolysis and gas separation techniques.

### 1. Technology of pyrolysis

The chemical reactions involved in the pyrolysis of hydrocarbons and particularly in the case of mixtures of a number of components are very complicated and only partly understood. Theoretical considerations can give no more than qualitative indications as to the direction in which further progress can be achieved. Only the practical experiment, whether on pilot plant or commercial scale, can provide the necessary reliable data for plant design or accurate performance prediction.

It is, therefore, understandable that technical progress in pyrolysis has been gradual and has extended over a lengthy period.

It may be said that the technique of pyrolysis of ethane became developed about ten years ago. Reaction conditions and optimum yield pattern obtainable, for which the data shown in table 4 are representative, have not changed materially since that time.

The pyrolysis of naphtha, however, requires rather a different set of conditions since the reaction rates of the hydrocarbons of higher molecular weight are many times greater than that of ethane. The realization of the theoretically most desirable conditions for maximum ethylene yield, which are a very short residence time and a high temperature of reaction, combined with a low pressure, or low partial pressure, met constraints of a technical nature, whereas the advantages to be gained by overcoming them could not always be proven in advance. Consequently, a step-by-step development took place, as a result of which an increase in ethylene yield for a feedstock like a normal paraffinic light naphtha (100°C ASTM end point), from 18 to 28 or 30 per cent wt on feed has been observed in the past ten years. This has been inade possible by gradual improvements in:

(a) The quality of available materials of construction for the reaction tubes, the tube supports, the furnace brickwork;

(b) The design of radiant box and lay-out of the reaction coil in this box;

(c) The design and arrangements of the burners for better heat transfer control.

The following table compares two sets of pyrolysis data; the first column showing yield data for an older furnace design, the second column for a very recent design, both cases using approximately the same feedstock.

As a result of these developments in pyrolysis, it is evident that the operating costs of the subsequent gas separation plant per unit production of ethylene could be decreased substantially since such an important increase of the ethylene concentration in the feed gas had been achieved. In this connexion it is important to note that, despite the higher conversion, the ratio between tail gas and ethylenc production came down from 0.81 to slightly below 0.6.

As far as the production of by-products is concerned, the following remarks are relevant when comparing the above two cases of different severity of cracking:

#### (a) Propylene

The rate of increase in propylene demand has fallen far short of that for ethylene. In most locations it is, therefore, quite acceptable and even desirable that the relative yield of propylene to ethylene has been dropping gradually in the course of the years.

#### (b) Butadiene

Butadiene is usually the more valuable component of the  $C_4$ -stream. At the same time that a decrease in total  $C_4$  yield at higher severity operation had occurred, an

TABLE 8. YIELD DATA FOR LIGHT NAPHTHA PYBOLYBE

	Per	a	ψ/	-	fe	vəl				Older design	New denig
	-										
Tail gas .						,				t4.9	17.8
Ethylana .										18.3	30,0
Ethene										7.5	4.2
C. Rection										t9.2	17.5
C. Insulion										12.2	9.7
Jacoline .										24.4	18.6
had all .										t.5	2.2

increase of the butadiene content in the  $C_4$ -fraction was achieved. Butadiene concentrations of between 40 and 50 per cent wt can be reached for the high-severity operation as compared with some 25 per cent wt in the older yield pattern. Consequently, the relative production of butadiene to ethylene underwent only an insignificant change.

#### (c) Pyrolysis gasoline

The quantity of pyrolysis gasoline produced is reduced from 1.44 to 0.62 relative to ethylene. In those locations where the gasoline can be used as a motor gasoline blending component and in this way contributes to the economy of operation, this will be seen as a disadvantage. The gasoline has to be stabilized, however, i.e., the diolefins have to be removed by hydrogenation before it is suitable as a motor gasoline. In most instances, therefore, the price obtainable for such a gasoline, after subtraction of the treating costs, is not high enough to outweigh the other strong advantages of high severity cracking. It should be noted in this respect that the aromaticity of the gasoline, and hence its value, normally increases with higher severity of cracking.

Apart from making it possible to obtain a generally more favourable yield pattern, the developments in furnace design have also resulted in capital savings - by stepping up the ethylene output of a furnace and by reducing the cost of construction and in an improved heat economy.

With regard to the latter point, a major step forward was made when the procedure for quenching the furnace effluent gas by direct contact with water or oil was abandoned some six to eight years ago in favour of a system in which a substantial part of the heat contained in this gas was recovered in the form of steam. Earlier designs provided for indirect heat transfer to the boiler by means of an intermediate heat carrier, such as Dowtherm. These systems could deliver steam at a pressure level of up to 20 atm, limited as they were by the maximum allowable temperature of the heat carrier. In later designs, direct steam raising was adopted, which had the additional advantage that for the same total heat recovery a much higher steam pressure could be achieved. The additional energy available in this steam could be utilized by being passed through a turbine with exhaust to dilution steam pressure level. The generator, driven by the turbine, could in this way produce more than one-third of the total power requirements of the gas separation plant. Alternatively, one or more of the main compressors could be directly steam turbine driven.

It is evident that material cost savings are made possible with these improvements in heat oconomy, since all dilution steam and a substantial part of the power requirements can now be derived from waste heat.

### 2. Technology of gas separation

In contrast to the major reduction of energy costs p.r unit of sthylene produced, resulting from improvements in pyrolysis technique as discussed in the provious paragraph, the effects of improvements in the technique of gas separation are modest. Energy requirements in gas separation have nevertheless been reduced but these reductions are mainly due to influences on which improvements in the gas separation process have had hardly any bearing. Such influences are:

(a) The substantial increase in ethylene concentration of the feed gas, a factor which has already been mentioned before:

(b) The large increase in average plant size which was conducive to

- (i) Improved efficiency of the major gas compressors and which made possible the economic use of steam turbine drives for these compressors;
- (ii) Reduction of relative cold losses through insulation, on account of the decrease of surface-to-volume ratio, inherent in size increase;
- (iii) Reduction of friction factors in lines and valves, also inherent in size increase.

However, some contribution has also been made by improvements in processing techniques, of which a few examples may be mentioned:

(a) Improved selectivity of acetylene hydrogenation catalysts. Whereas in the older designs a two-step hydrogenation was required, one before the demethanizer and one after the de-ethanizer in order to reach the low acetylene concentrations required by most ethylene consumers, presently available catalysts allow of hydrogenation in one step, either before the demethanizer or after the de-ethanizer. Different types of catalyst are produced for these variants;

(b) Development of more accurate physical data on phase equilibria, particularly in the low temperature/ high pressure region, so that separation columns could be designed with marrower margins on reflux quantity and tray numbers to fulfil the required product specifications;

(c) More extensive use of multiple-stream heat exchangers, by which cold could be recovered to a maximum extent from each single product stream;

(d) Development of reliable gas expansion turbines for additional refrigeration duty in the demothanized top gas below the lowest temperature level of the ethylene refrigerant cycle.

#### 3. Future trends

There are sound theoretical grounds for the view that a further spectac-slar increase of the ethylene yield in light naphtha pyrolysis is not to be expected. At the higher temperatures and shorter residence times required to obtain a favourable shift in the pyrolysis reactions towards higher ethylene yields, the dehydrogenation of ethylene to acetylene is rapidly accelerated. Hence, although small advances may still be achieved, it appears unlikely that commercial yields will exceed 35 per cent wt in the future.

From the analysis presented earlier in this section, it will be understood that the likelihood of further major advances in gas separation is even less than in pyrolysis.

The underlying reason is that low temperature distillation processes have been developed to a high degree

of thermodynamic efficiency and are producing high purity products.

In combination with a modest increase in ethylene yield from pyrolysis, there is scope for no more than a fairly marginal improvement in energy consumption.

Finally, there is but little doubt that continued inflation will act as a moderator to any further cost savings that might occur in the process for producing ethylene from naphtha.

#### IV COST MOVEMENTS IN FTHYLFNF MANUFACTURF

In the foregoing, two main factors, namely the economic factor and the scale of manufacture and technical progress, have been shown to be responsible for the major reduction in ethylene cost over the past ten years or so.

The magnitude of this cost reduction can hardly be better illustrated than by comparison of the price of ethylene in 1956, some pounds sterling 80 per ton, with that from a large, modern plant of about pounds sterling 40 per ton at the present time.<sup>1</sup> An analysis of the underlying cost reduction in quantitative terms is, therefore, of considerable interest.

The two main factors cannot be fully separated in their effect on ethylene cost, since they show a degree of interrelation. A case in point is the reduction in capital cost for gas compression.

In a small plant, below about 25,000 t.p.a. of ethylene capacity, all compressors have to be of the reciprocating type, since for the small duties involved no efficient centrifugal compressors can be built. Above a capacity of some 60,000 t.p.a. all three main compressor duties can be made centrifugal. Since the reliability of operation of centrifugal compressors allows the installation of single machines for each duty and no spare machines are required, as would be the case with reciprocating compressors, it is seen that increased size of plant enables a better technical arrangement to be made; saving capital and thus cost.

However, despite this interrelationship, it is fair to say that the technical improvements have affected mainly the variable costs of manufacture, whereas the factor of size has influenced in particular the fixed costs.

For understandable reasons, the cost data used in the following analysis have been taken from the literature. However, the trend shown by these figures is fully in line with experience of the Shell company as well.

#### 1. Energy requirements

The developments discussed in the previous sections — mainly those in pyrolysis technique — have led to considerably reduced energy, i.e., utilities requirements per ton of ethylene produced in a modern plant, compared with a plant of older design.

In table 9, these concumption data are compared for a 20,000 t.p.a. of older design, conforming to the yield structure shown under the heading "older design" in

<sup>&</sup>lt;sup>1</sup> Burepean Chemical Nove (Databar 18, 1963).

TABLE 9 UTILITY REQUIREMENTS PER TON OF ETHYLENE PRODUCED

en en com en	Unde	0 <b>1de</b> r design 60,000 t.p.a	Neadorn design GUU,000-1.p.a
Electric power	10 <sup>4</sup> kWh	2.2	0.6
Boiler feed water	ton	1.8	0.8
Fuel gas Cooling water (15°C temp	10 <sup>e</sup> kcal	9.6	6.0
rine)	10 <sup>e</sup> tons	1.1	0.25

TABLE 10. UTHATY CORTS PER TON OF ETHYLENE PRODUCED.

		Cost in plane of			
	Unit cost	20,099 t.p.a.	200,100 i.p.a		
Electric power	£4.17	£9.2	£2.5		
Boiler feed water	£0.15	£0. 1	±0.1		
Fuel gas	20.7	£6.7	£4.3		
Cooling water	£2.5	£2.8	£9.6		
Instrument air, etc		p.m.	p.m.		
TOTAL, utilities £/Ion		£19.0	£7.5		

\* J. Chrones and J. C. James. Economics of ethylene production from light apphthas, Institute of Petroleum Journal: 46: 337 (1966).

table 8, and a modern 200,000 t.p.a. plant for which the yield pattern shown in the column headed "new design" is representative.

Table 10 expresses these consumption figures in costs per ton of ethylene.

Basic utilities costs have not moved materially during the period. Hence, for both plants the same unit costs have been assumed. It should be added that the figures shown are averages, and that they may vary according to local conditions.

#### 2. Capital costs

The development of the capital cost of ethylene plants during the past ten years or so presents an extremely interesting picture.

Initially, until about 1957, the investment cost for a plant of given size increased from year to year, following the general trend of increasing index figures for installed plant.

By that time, the technological improvements achieved in othylene manufacture and discussed previously began to event their influence on capital cost. The result was a not decrease of plant cost (for a given capacity), which continued until last year. The savings achieved more than effect the inflationary cost increases which ecsured continually during the period.

In figure III the movement of the index of construction soat is represented in graph form. Ethylene plant investment costs have been virtually constant from 1963 to 1964, and it is likely that they will increase again in the future.

Of particular importance is the investment cost per annual ton of installed capacity, since this figure is at the root of all capital related items in the manufacturing cost breakdown.

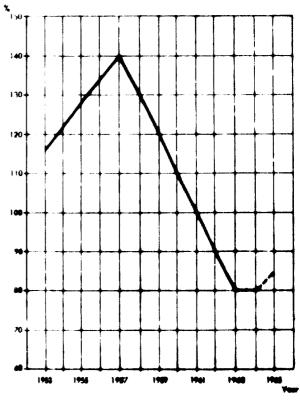
Figure IV shows the movement of the investment per annual ton. Curve A represents the picture that would arise if no other changes in the cost of ethylene plants had occurred than those shown in figure 111.

However, apart from the falling cost for a plant of given capacity since 1957, also the capacity of units built has steadily increased. Since capacity increase can be achieved by increase in size of equipment and at higher capacities, the advantages of centrifugal compression can be used to the full, capital increases far less than proportional with capacity. Consequently, investment cost per annual ton comes down with increase in size.

When this factor is also taken into account, curve B in figure IV results, showing that capital cost came down from £105 to some £35 per annual ton of ethylene in the period from 1955 to 1964.<sup>2</sup>

Although it is difficult to predict with accuracy, it may be expected that the installed cost per annual ton of ethylene capacity will remain fairly constant in the

\* European Chemical News (May 10, 1963).



Piguro III. Index of expited easts for edgelone plant (1986 = 1886)

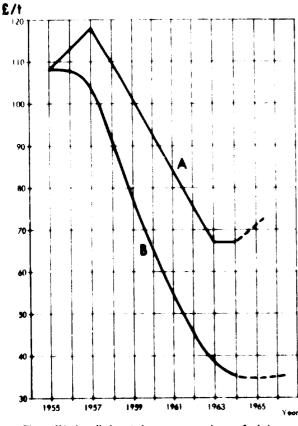


Figure IV. Installed capital cost per annual ton of ethylene

future, at a level of £35 to £40, since the advantage of further increasing plant size is likely to be balanced by the rusing trend of index of construction figures.

#### 3. Net feed cost

Since even with high severity cracking, ethylene yields are not materially above 30 per cent wt on naphtha, it is evident that — apart from the naphtha price — the credit for the by-products is an extremely important factor in ethylene production.

The values which the by-products — tail gas,  $C_s$ - and  $C_s$ -fractions, gasoline and fuel oil — will command will vary from one location to the other. A balanced utilization of these by-products, commanding for several of them a premium above their fuel values, is essential for economic ethylene manufacture.

With naphtha currently available at about £7.5/ton, the average situation in western Europe works out at a net feed cost of some £5/ton of ethylene.<sup>3</sup>

For a plant operating some ten years ago with the yield structure then attainable, not feed cost was of the order of £15/ton of ethylene, owing subinity to the higher naphtha price of about £10/ton.

It is not to be expected that the future will see much further fall in naphtha prices. With increasing demand for naphtha as feedstock for ethylene and for reforming to produce hydrogen or town gas, naphtha has virtually ceased to be a "by-product" of refinery operations.

#### 4. Cost comparisons, past, present and future

Applying the data developed in the foregoing, manufacturing cost comparisons can now be made between old and modern ethylene plants.

For this purpose, a plant of 20,000 t.p.a. operating in 1955 and a modern, 100,000 t.p.a. plant in 1965 were selected, based on the consideration that plants of these capacities dominated and will dominate the scene in the years indicated.

In years to come a further increase in the capacity of ethylene plants will be experienced and the assumption is made that by 1975 plants of the order of 200,000 tons capacity will be dominating. Such a plant is, therefore, included in the comparison.

The dramatic cost reduction from the 1955 plant to a large-scale modern one is most striking. This trend would continue when in future years the advantages of large-scale production become increasingly utilized, if no inflation would occur (table 11, column 3). However, if the assumption is made that wages will increase by 3 per cent and plant construction costs by 4 per cent per year, column 4 shows that ethylene cost will remain virtually constant despite further increases in scale of manufacture. In the light of recent experience in western Europe, these assumptions appear to be quite reasonable.

Nevertheless, even constant costs in the face of strong inflationary pressures, would be no mean achievement for the industry.

The data shown in this table strongly emphasize the advantages of large-scale production. It should be emphasized, however, that these can only be realized if a high plant loading — close to capacity operation — can be sustained. The high share of the fixed costs in the total manufacturing cost will be responsible for a steep increase of the latter under conditions of sev. — underloading of the plant.

#### V. TRANSPORTATION COSTS OF ETHYLENE DERIVATIVES

The desire to produce petroleum chemicals in a location where abundant raw material is cheaply available, even if there is no or only a small local market, is all but natural.

Examples would be the manufacture of ethylene from condensate of natural gas in Algeria or from ethanc extracted from natural gas in, e.g., Kuwait. There is no doubt that in such locations ethylene could be produced cheaply in large-scale facilities, at costs comparable with those shown in table 11, or perhaps even a little cheaper.

The othylene would, however, have to be converted into marketable products and shipped to the existing markets. It is, therefore, interesting also to see how the transportation costs of the main derivatives have moved

<sup>&</sup>lt;sup>3</sup> CI. for engagele, European Chemical News (Polerany 22, 1963), which shows a net field cast of £2.9 per ten of othylane.

TABLE 11.	COMPARISON	OF	ETHY! SINE	MANUFACTURING	CO575
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i per ton of ethniane	Old plane 1963	Modern pient 1965	Future plant 1975 200,000 1.p.a.			
	30,0 <b>0</b> 0 i.p.a.	100,000 i.p.e.	No inflation	With inflation allowance		
Net feed cost	15	5	5			
Chemicals	1	1	i			
Utilities	19	10	8			
Variable	35	16	14	14		
Labour, overhead	11	4	2	3		
Maintenance	4	2	1	2		
Depreciation	31	10	8	12		
Fixed	46	16	11	17		
	81	32	25	31		

over the years. Marine transportation of ethylene itself, although technically feasible, is not done and is, therefore, left out of consideration.

1

11

Study of the subject revealed that in the period between 1950 and 1964, transportation costs of chemicals from the United Kingdom to a Persian Gulf destination have, on the average, increased by about 100 per cent. The increase ranges for individual products between 50 and 135 per cent.

The case will thus not be overstated, if it is postulated that the shipping cost for low pressure polyethylene and for ethylene glycol has increased by 50 per cent during the period. The following picture then emerges:

With regard to the major price decreases for ethylene based products over the same period, it is clear that transportation costs constitute at present a far higher

TABLE 12. SHIPPING COSTS BETWEEN THE UNITED KINGDOM AND PERSIAN GULF

1 per	Im					Early 19 <b>3</b> 0s	1964
Polyethylens, packed						12	17.3
Ethylene glycol drams						13	18.5
Ethylene glycol huik.						1	10-12.9

proportion of the value of the chemical being shipped than they did some ten years ago.

It is also relevant to compare the cost of shipping with the base material element in the cost build-up of ethylene and its derivatives. It will be seen that the former dominates.

#### **VI.** CONCLUSIONS

The main conclusions which can be drawn from the present paper are summarized here.

- Manufacturing costs for ethylene will come down from a level of about £80/ton in a 20,000 t.p.a. plant in 1955 to around £35/ton or even lower for a largescale (100,000 tons or over) plant of modern design, when suitably loaded.
- 2. These cost reductions have resulted both from technical progress and from the very rapid growth of the market for ethylene based chemicals, which have enabled ever larger plants to be built, with attending economics of scale.
- 3. It is not expected that ethylene costs (and prices) will decrease further in the future. The expectation seems justified that further advantages of scale will balance inflationary cost increases.
- 4. Over the period considered, the shipping costs of ethylene based chemicals have increased by, at least, 50 per cent.

# 12. OLEFINS VERSUS ACETYLENE Competitive raw materials for the petrochemical industries in developing countries

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#### INTRODUCTION

Petrochemicals are assuming increasing importance in the world's chemical industry. In the United States of America they represent about one-third of the total volume of all chemical production, which is now about 100 million tons annually. This is almost one-half of a ton of chemicals per person per year; and in the rest of the world, the consumption is less — possibly averaging, in the developing countries, only a few per cent of the amount used in the most highly industrialized countries. The problems faced in each country are quite different as regards planning for chemical industry. Available inaterials and consumer demand are the most important considerations; others may even include the possibilities of manufacture for export.

The choice of raw materials for this increasingly important industry must always be considered very carefully, even in the United States where petrolcum products and coal are relatively cheap; and there is also relatively cheap electric power available for making calcium carbide, and thence acetylene, one of the prime sources of what has come to be known as "petrochemicals". This balancing of costs between source materials for a hydrocarbon based chemical industry is even more important in those countries where these materials will have different ratios of relative costs; with one or the other in insufficient supply and necessarily imported or replaced by the other. Also, while material and capital costs are relatively low in the highly industrialized countries --- particularly in the United States of America - labour is relatively expensive.

The routes to the production of any chemical necessarily depends upon the raw material which may be used; and the costs of the productions vary also. Primarily, it is necessary to consider acetylene, ethylene, and the more recently important propylene, in their competivive roles as raw materials. The economics and technological aspects of the supply and application possibilities of acetylene as compared to the olefins in the chemical process industry are of the utmost importance throughout the world, but especially in developing countries. It is desired to consider the availability and the cost of making each of these raw materials in the relatively smaller units which may be desirable for starting production in developing countries.

Considering first only the present economics in highly industrialized countries such as the United States of

America, the Federal Republic of Germany, the United Kingdom of Great Britain and Northern Ircland, or Japan, an evaluation may be made of the chemical endproducts coming from the competitive raw materials by different routes and ready for further synthesis, polymerization, or other chemical processes into consumer goods. The relatively high price of acetylene of 10 to 12 cents per pound from calcium carbide, is a major deterrent to the increased use of this versatile raw material, even though its production amounts to almost 100 million pounds in the United States of America - about 80 per cent of it being used in chemical manufacture, and the rest as a special fuel, illuminant, etc. Ethylene, at an average price of about 3 cents per pound in the United States of America, is the cheapest available starting material for chemical synthesis and is, by far, the largest volume of aliphatic material for petrochemical use, excluding, of course, crude stocks and natural gas used for fuel. Ethylene production capacity in the United States of America may be estimated at from 7,000 million to 8,000 million pounds per year, and is still above the production demands. In the United States, it comes largely as a by-product of cracking to obtain gasoline, because of the tremendous amount of motor fuel required on the roads of the great inland areas. In many other countries, ethylene comes as a main product in cracking petroleum distillates such as naphtha.

In developing countries, as also in the United States of America, the question of using acetylene, whether from carbide or from natural gas, must be balanced against the use of ethylene. Some aspects of the chemical interrelation of the important products which may be made from acetylene and the olefins as raw materials will be considered, as well as the competitive aspects of production of the chemicals which may be made from either the one or the other. Also, the economics as well as the technology of such manufacture must be evaluated and compared under the different conditions which obtain in each developing country without the large consumer markets, which will be expanded as the country develops economically. Natural gas, crude oil, and water power for electrical energy, may be regarded as the basic raw materials in view of their relative abundance or cheapness. Coal for coking, the production of acetylene from the carbide which is produced from the coke or from the methane which is produced from the coal gas, may also be considered. In every case of competitive processes or raw materials, an exact analysis is essential.

#### BACKGROUND OR HISTORY OF THE PROBLEM

It is worth while to consider the history of petrochemical development in mature industrial countries, in order to understand the part of this history which must be repeated in a country developing towards the maturity of its chemical industry during the latter half of the twentieth century. Those parts of the history which may possibly be followed should be noted along with those steps and pitfalls which may be eliminated in building new petrochemical industries today, hased on the experience of the past.

Acetylene as such is a most useful fuel for specialized uses, notably the acetylene-oxygen torch for cutting steel. Acetylene for this purpose is urgently needed everywhere; and where not locally made, solid carbide is usually imported rather than acetylene in cylinders. Acetylene is then produced from carbide, in simple, continuously operating units in all sizes down to that required for a bicycle headlight.

The lirst major use of carbide, after supplying acetylene as a specialized fuel, was also not related to its present major uses as a petrochemical starting point. The first large chemical production of carbide was for calcium cyanamide, the first form of synthetic nitrogen fertilizer. Direct ammonia synthesis gives a cheaper fertilizer; and no more carbide plants will be built to make calcium cyanamide, certainly not in developing countries. In Japan, the United States of America and elsewhere, production facilities built for carbide to be used for ealcium cyanamide now produce carbide for acetylene --- a building block for organic chemicals. In a country such as Japan, with expensive fuel and small petroleum reserves but with abundant water power, a logical production has been calcium carbide, utilizing electrical energy to incorporate the considerable molecular energy which has been stored, first in the carbide, and then in the acetylene. The tremendous carbide industry in Japan produced the early petrochemicals there via acetylene; and during the Second World War, besides many chemical products, it even provided the synthesis from acetylene (via acetaldehyde, butylaldehydc, octanol to octane) of gasoline for fuels in fighter aeroplanes - 1,000 tons per day in one plant alone.

After the war, much of the possible acetylene production of Japan was available for the production of chemicals for consumer goods. Economic surveys indicated that the high cost of carbide furnaces and acetylene production thereby was necessary because of the lack of other feedstocks for petrochemical programmes; and the availability of cheap electric power indicated a relatively easy sequence for the emergence and expansion of a petrochemical industry based on acetylene.

In such non-industrial countries with available and undeveloped water power and with relatively little petroleum resources, such as Burma, a petrochemical industry might be based on acetylene. Carbide could be imported first; and the acetylene resulting therefrom would be used as the basis for the desired petrochemical manufacture. As the production developed and the financing was justified for the carbide complex, this would be built with the consequent elimination of the import of carbide.

Meanwhile, a very quick entrance into petrochemicals could be realized, with low investment of time and money necessary before the first petrochemicals were made. Ultimately the acetylene might be made from petroleum or natural gas, as hydrocarhon resources were found to be available.

In the United States of America, the development of ethylene as a raw material during the last thirty years has required merely the processing of the off-gas streams from the cracking of petroleum stocks to produce gasoline, and there has always been more available from this source than could be utilized chemically.

With the intensive efforts towards national selfsufficiency in petroleum products, the same route via ethylene will follow in some developing countries, many of which are determined to install petroleum refineries, and later cracking units. On the other hand, ethylene may also be produced in relatively small plants as a principal product of cracking petroleum distillates, which would come cither from a petroleum refinery in a developing country before a petroleum cracking operation was justified, or from imported naphtha. This would also offer a relatively low-cost investment in time and money for the basic stream of raw material, in this case, olefins. Cracking, either for the production of gasoline or for production of olefins, also gives propylene, a raw material for petrochemicals of important types being developed in this decade.

Similarly, the cracking or dehydrogenation of petrolcum distillates, and especially natural gas, is now being developed as a source of acetylene; and it is anticipated that considerable progress will be made in the next year or so towards the reduction of the price of acetylene coming from either natural gas or liquid petroleum feedstocks.

These natural gas and petroleum-based acetylene processes and plants have necessarily grown up competitively in the industrial countries with both the carbide production of acetylene and, particularly, the ethylene coming from cracking operations. However, in developing countries, where planning can start with the available experience of the more mature countries, it would be necessary to evaluate the cost of acetylene from carbide or based on either natural gas, if available, or petroleum distillates, either available from refining operations or imported.

In programming a petrochemical industry other conditions are most important in relation to raw materials other than those derived from the petrochemicals. Thus, the availability of a caustic-soda industry, of a sulfuric acid plant, and of numerous other less basic materials must be considered.

Furthermore, the interrelation of the several products to be made is always important in chemical production, and the balancing of demand of one item against its productive facility is almost always influenced by the production of by-products. For example, in the production of acetylene, pure hydrogen may be made simultaneously. This may be made into ammonia and other fertilizers; but the amount of ammonia from the hydrogen would probably not be commensurate with the amount of acetylene which might be utilized in the country. Acetylene has been evaluated, usually, at about 9 to 12 cents per pound in the United States of America, based on carbide, and more recently on hydrocarbons.

In the Wulff thermocracking process, there is a regenerative furnace which supplies heat to the hydrocarbons to crack them to make acetylene as well as ethylene and other products. Temperatures from 900°C to 1,300°C, with time of contact of about 1/20th of a second, give a product gas which is cooled in the furnace and then by sprays of water. A major gas-separating operation is necessary. Simultaneously, both ethylene and acetylene are produced at an average cost of probably more than 5 cents per pound. If the lower cost of ethylene coming as a by-product from gasoline production is considered, the acetylene cost is, of course, considerably more. Various factors have prevented wide commercial success of the Wulff process.

The BASF process used in many countries oxidizes methane from natural gas, coke ovens, or other sources, with oxygen at a flame temperature of about 1,500°C, followed by rapid quenching, gas separation, etc. Production costs are probably in the range of 7 to 8 cents per pound, and plant costs are relatively high. Much of the engineering design is usually left to the licensers of the BASF process, and there has been a diversity of experience in practice.

The SBA process operates somewhat similarly to the BASF reactor or burner. There is a divergence in the gas purification processes, and a modified burner. The SBA will utilize feedstocks of C-3 up to C-12. The costs are probably in the range of the BASF.

The Montecatini Partial Combustion Process, which operates at higher pressures of about four atmospheres, utilizes some steam. The production cost is probably in the range of the other partial-oxidation processes, although at least one of the major users has been less than satisfied with the operation and its costs.

The DuPont Arc process is a modification of an electric arc discharge, which has been used by others. Because of the large variation of temperature — from 1,500°C to 3,000°C — optimum conditions, and hence optimum yields — which would be dependent on one best temperature — cannot be expected with this or with other of the arc, or so-called plasma processes.

Currently, a large number of companies and laboratories are working to develop methods of making acetylene cheaper. Basically, the large increase in reactivity of the hydrocarbon molecule with the triple bond makes acetylene more valuable than ethylene with a double bond; and much more valuable than methane with only single bonds. Thus, the monetary value is also greatest for acetylene. The obvious need is for some means of supplying considerable energy for rapid heating of the feedstock to a high reaction temperature, and the addition of the molecular energy, because of the triple bond. Then very rapid cooling is necessary to stop side reactions. Heat transfer problems are difficult because of the short time intervals involved.

The aim in acetylene production is to convert essentially all of the hydrocarbon feedstock to acetylene and hydrogen. This must be done at a high temperature and at a very low time of reaction. Intermediate temperatures favour side or reverse reactions; hence, rapid cooling is essential. The product stream would thus, ideally, contain only acetylene and hydrogen --- no by-products and no unreacted feedstock are desired. An optimum process might reduce by a major part the plant cost by eliminating most of the gas separation equipment. The separation of the acetylene from the hydrogen may, following such an ideal reactor, desirably be done chemically through the interaction of the acetylene with other materials, e.g., water to give acetaldehyde, hydrogen chloride to give vinyl chloride or chloroprene, etc. The hydrogen which results after such removal of the acetylenc may be substantially pure, and has a value per cubic foot, for synthesis of ammonia or other uses. considerably in excess of that of the natural gas which may be used as the feedstock. On a molar or volumetric basis, it may be several times or more the volume of the gas or vaporous feedstock going in the reactor.

The consideration of such an optimum process is worth while, because it allows the placing of the technical and economic limits in the evaluation of basic chemical costs for synthesis of petrochemicals.

All of the desired results of this optimized hypothetical reaction have been approached in a laboratory operation under Professor Happel and Dr. Kramer in New York, utilizing feedstocks varying from methane to naphtha, a pressure range of over tenfold, and carefully controlled high temperatures at nearly isothermal conditions throughout the reaction zone. This work and corroborative laboratory work on the process by others indicates that a substantial solution of the economic and technological problems is possible, if similar results are obtainable on a large scale. Small pilot plant operation in the United States of America and elsewhere has been equally optimistic. The complete range of conditions which has been encompassed in the kinetic survey allows the prediction, understanding, and setting of the exact operating conditions for optimum plant use. The process, simple as it is, is the basis of two granted United States patents --- 3,156,733 and 3,156,734, numerous patent applications in the United States of America, and a score of other countries.

In this laboratory work, there is used neither an arc, a plasma jet, a partial oxidation, nor regenerative heating, so that the plant operation should be of the utmost simplicity and the plant, itself, of minimum cost. The thermal and chemical energy requirements have been supplied electrically; and the calculated plant costs have been based on similar supply, although it may be possible to add the required thermal energy from the burning of a fuel and this may reduce the cost substantially.

Typical chemical reactions for typical hydrocarbons to give acetylene and hydrogen are as follows:

2 CEL <sub>4</sub> → C <sub>2</sub> H <sub>2</sub> + 3 H <sub>5</sub>	
$C_{4}H_{10} \rightarrow 2C_{1}H_{1} + 3H_{1}$	
$C_{10}H_{01} \rightarrow 5C_{2}H_{1} + 6H_{1}$	

The chemical conversion of the hydrocarbons has been almost complete under the optimum conditions in the laboratory unit, on which many hundreds of experiments have been made; and the conversion to acetylene has been as high as 90 per cent in a single pass in a reaction time of less than a thousandth of a second. It has been found that in some cases it is desirable to have an optimum disappearance of the hydrocarbon with a slightly lower yield, in order that none of the feedstock may be present in the product gas, which will then contain only acetylene and hydrogen. Under such conditions, it is possible to obtain ethylene contents below one-tenth of one per cent. Higher acetylenics are present in an amount which is also below one-tenth of one per cent.

Analysis of the products has been based on chromatographic and spectrophotographic analytic methods. One typical product gas stream has analysed:

Acet <b>ylene</b>	Ethylene	Hydrogen	Methane	Higher acetylanics
21.1 mole %	0.0 mole °°	74.0 mole %	4.9 mole "。	Less than 0.1 mole %

As noted, if the operation is conducted to obtain a somewhat lower percentage yield by practically destroying this residual methane, and if the acetylene is chemically removed from the gas stream to make the desired product, the gas-separation operation almost disappears. Alternately, a recycle will, of course, give an even higher yield of acetylene.

From the hundreds of runs which have been made, it is now possible to fully demonstrate the optimum conditions of feed rates, time, temperature, and pressure for each feedstock. Complete kinetic correlation has been obtained on a master chart of the conversion and yields, with temperatures, pressures, space velocities, etc. Scale-up to plant size has been based on the desire to determine the essential features of heat transfer which are important problems in the plant design, and also to utilize a modulus of design such as a single tube which, after heat transfer experiments have been made, may be used in large numbers for the entire heating unit of an evaporator. It is expected that the industrial plant will be simply a multiplication of numbers of modules of the pilot plant reactor, because of the sureness in scaling up homogeneous gas reactions.

Most of the work has been done with methane because of the ready availability of natural gas almost anywhere in the United States of America, and in many other countries. Other hydrocarbons than methane, both saturated and unsaturated, have also been used quite satisfactorily as feedstocks, up to the lower naphthas. Both pure materials and mixtures have been used. It has been found that the optimum values of temperature, pressure, and space velocity for one hydrocarbon vary somewhat from the optimum values of its homologues. Thus, for a given mixture of hydrocarbons (i.e., a particular analysis of naphtha or natural gas) the operating conditions must be chosen to give the optimum for the weighted average of the molecular weights of the several components of the mixture.

Methane in the form of natural gas is a very suitable feedstock, but other gas streams, such as refinery gas streams, containing substantial amounts of oletins, cokeoven gas after separation of more readily condensable constituents, and others, may be used, often without separation of the components. Thus, for example, the presence of ethylene is not objectionable since it goes out almost quantitatively with acetylene; it has been found possible to produce mixtures of ethylene with the acetylene product, as has been demonstrated by the kinetic studies and charts which have been developed — and as has long been known. However, this mixture must then be separated by processes which add to the cost.

The charts of kinetic data of the reaction of the lower saturated hydrocarbons to produce acetylene and hydrogen, which have been obtained from careful laboratory studies, make it possible to understand the interrelation of the controlling variables. They also show why this process gives such high yields compared to the maximum yields which can be produced under the operating conditions of the other processes, such as those using partial oxidation. These studies have been made over a range of temperatures and pressures and at widely differing space velocities or times of reaction. They have also included butane and decane as representative of higher hydrocarbons, which might be more readily available under some conditions.

In work with higher hydrocarbons, the losses are slightly greater and the conversion may be 5 to 10 per cent less.

With the over-all kinetics of the reaction of formation of acetylene from hydrocarbons now fairly well understood, it may be possible to define the optimum conditions which should be maintained and controlled in plant units. Thus, it has been possible to develop the probable minimum costs of acetylene coming from natural gas or petroleum fractions up to naphthas. This gives a base or point of reference for estimating what should soon be available commercially.

Modifications of the basic furnace design used in the fundamental kinetic studies in the laboratory work have resulted in the design of a small reactor which may be operated continuously without trouble with carbon formation. This work has indicated some of the parameters and problems for scale-up. One of the major United States producers of acetylene from hydrocarbons has supported pilot plant work in return for the rights to build the first large plant using this process.

Pilot plant operations based on these kinetic studies in Europe, Japan, as well as in the United States of America, have given results confirming the predictions of the kinetic studies, although these optimum conditions demonstrated in the laboratory have never quite been reached so far; and the conversions have been in the mid-80 per cent in a single pass, much higher, however, than those that have been achieved previously without this guiding understanding of the theoretical or optimum kinetic performance.

#### **ECONOMICS**

The very small-scale laboratory operation work was done to outline the optimum performance and to define the operating conditions which would give it. The larger pilot plant unit has given sufficient corroboration to make it possible to estimate roughly the size, and thence the cost, of the reactors and other parts of a production unit.

It is estimated that the plant costs will be relatively low because of the absence, or near absence, of an expensive separating plant for the product gas stream; also because of the relatively small size and inexpensive construction of the reactors — particularly if electric heating is used.

Only electric power, for the thermal requirements and the chemical energy tied up in the acetylene molecule, and cooling water are required, besides the input stream of natural gas, or other source of lower hydrocarbons. Naphtha fractions are more available and cheaper in many places.

A major plant has been designed and cost-estimated by engineers with much experience in such work. It will require both multiple and single units, for a range of production of acetylene of 25 to 75 million pounds per year. The cost of the plant, battery limits, might be from 5 to 8 cents per pound production of acetylene per year, depending on how much separation is required of the final gases to obtain the acetylene.

Thus, a 50-million-pound per year plant might cost \$2.5 million to \$4.0 million, and a plant for 10 million pounds, which seems a reasonable smaller-scale unit, might cost less than \$1 million. Lower figures indicate costs for a plant in which the acetylene is separated from the product gas stream by subsequent chemical reaction, while higher costs would include the plant cost for separating specification grade acetylene for sale as such.

It might be noted that the mixture of acetylene and hydrogen may be used without separation for oxyacetylene torches, for this market.

Beginning with methane as natural gas, valued at 20 cents per thousand cubic feet, with electric power at 0.6 cents per kilowatt, and with usual depreciation, amortization, maintenance, labour, and other charges, the cost of acetylene has been calculated as somewhat less than 5 cents per pound, if hydrogen is credited only at its heating value. However, since practically pure hydrogen is produced, it may usually be sold for other uses, e.g., ammonia production; and if it is valued at only 30 cents per thousand cubic feet, the cost of the acetylene goes down to 3.0 cents per pound. In those cases where natural gas is more expensive, hydrogen is also more valuable when it is required; and the acetylene cost would be even less. In any case, it would be desirable, although not essential, to construct a plant where the profitable use of hydrogen could be expected or planned. As always, when two products are produced, one may be regarded as the principal product; and here either hydrogen or acetylene may take that role.

From the successful operation on a small scale, this process may be regarded, however, as showing the possibilities which may be achieved either in the commercialization of this process or through the development of other acetylene processes by other engineers. The

purpose of this discussion is to indicate the relatively low price which acetylene may attain; and indications are that, under certain operating conditions, the cost might even be slightly less than 3 cents.

#### PETROCHEMICALS FROM ACETYLENE OR FROM ETHYLENE

The principal end products which are made from acetylene in the United States of America may be indicated. An approximation of the total percentage of acetylene used in each is indicated, this being of more interest than the absolute amounts or values of the product:

								1	Per cent
Vinyl chloride monomer									27.5
Neoprene.									21.0
Vinyl acetale monomer									
Acrylonitrile									14.0
Trichloroethylene									9.0
Miscellaneous chemical	pr	od	uc	15					8.0
Non-chemical uses									13.0

All of these, possibly, except neoprene, may be based on other materials, notably ethylene and propylene, under those conditions where economics justify it, depending on the relative price schedules of the competing raw materials, their availability, etc.

These materials are made from the 1,000 million pounds annual acetylene production at an average charge to the process for the acetylene of probably about 9 cents per pound. Considering the relative amounts of these materials which will be produced if it is possible to decrease the cost of acetylene substantially, there will be a radical change in the situation in the United States of America, where the volume of acetylene production has reached a plateau, while the volume of production of both ethylene and propylene is increasing very considerably. Thus, in the first five years of the 1960s, it is estimated that the acetylene production will not increase greatly, while the ethylene production will go from about 5 million pounds to about 7 million pounds under the present range of prices. Decreasing the acetylene cost to 5 cents per pound will greatly increase the total usage, as it will increase the amounts of those chemicals made from acetylene, which chemicals can also come from the olefins.

It is safe to say that, with a decrease of acetylene only to the 5 cents per pound range, i.e., a cost basis at which it must be charged into chemical processing at a cost per pound equivalent to that of ethylene, all of these materials presently made from acetylene may be made more cheaply than if made from the olefins. Usually the efficiency and simplicity of the process for the production of a chemical which can be made from either acetylene or ethylene will show that the yields and the plant cost are more favourable to production from acetylene.

#### VINYL CHLORIDE

As regards the volume of production but not the total value of the product, the largest user of acetylene is, of course, vinyl chloride. The classical process utilizes acetylene, plus dry hydrogen chloride. More recently, vinyl chloride has been produced from ethylene plus chlorine, to give ethylene chloride, which is then cracked to give vinyl chloride, plus hydrogen chloride. The processing cost of this two-step process is considerably greater than that from the one-step acetylene-based process. However, if both ethylene and acetylene are available, the hydrogen chloride formed from the cracking of ethylene dichloride may then be immediately added to the acetylene which is available. Major producers in the larger industrial countries are operating such integrated plants.

A major competitive advantage being shown for ethylene-based vinyl chloride is the use of any one of the several commercial processes for what is known as "oxy-chlorination". In this process, ethylene chloride is produced by oxy-chlorinating ethylene with hydrogen chloride, rather than chlorinating ethylene with chlorine. The ethylene-dichloride, when it is pyrolyzed, gives hydrogen chloride, which is used to oxy-chlorinate additional ethylene dichloride from the feed stream of ethylene.

The processing steps and plant are, however, as yet not standardized, and much more expensive. With ethylene and acetylene at the same base prices per pound, the vinyl chloride will cost less by the direct addition of acetylene and hydrogen chloride, than by the oxychlorination of ethylene with hydrogen chloride and the pyrolysis of the ethylene dichloride.

With 4.5 cents acetylene, and 1 cent hydrogen chloride, it should be possible to make vinyl chloride for less than 3.5 cents per pound. Regardless of the source of the vinyl chloride, the cost of polymerizing it is about 3 cents per pound, which gives polyvinyl chloride in the range of 6.5 cents per pound. With acetylene at even lower costs --- as will be possible with the development of the optimum process --- the cost of manufacturing polyvinyl chloride may be between 4 cents and 6 cents per pound. This would only be feasible for a very large and advanced enterprise; whereas, in developing countries, it might be expected that the cost in the smaller plants would be somewhat more. However, the relative costs in the use of ethylene or acetylene will be the same; and the simpler production from acetylene may be especially attractive.

#### NEOPRENE OR CHLOROPRENE

As noted above, this material, a relatively higher priced elastomer based on acetylene and hydrogen chloride, has only been made from acetylene. Until 1959 when vinyl chloride overtook it, it was the largest user of acetylene in the United States of America. The relatively sensitive process has recently been mastered by two producers in Japan, one quite independently. Almost half again as much acetylene goes to make a pound of this product as to make a pound of vinyl chloride; hence, a reduction of acetylene price will reduce the cost per pound more; although the selling price, which is relatively high for this profitable polymer, would not be affected by nearly as great a ratio. It has been estimated that, even in the United States of America, this production

might, however, be stimulated by as much as 40 per cent with lower cost acetylene. The lower priced raw material might even encourage new sources of supply.

#### VINYL ACETATE MONOMER

This material of rapidly increasing interest is used to make four major types of resins of considerable importance in the latex-paint, adhesive, textile, automotive safety glass and vinyl resin fields. These products are: polyvinyl acetate, polyvinyl butyral, polyvinyl alcohol, and vinyl chloride-vinyl acetate copolymers. More recently, there has been added to this list the ethylenevinyl acetate copolymer, which has potential importance as a synthetic rubber. The simple method of production of the starting monomer, vinyl acetate, depends on acetylene, and, with lower cost acetylene, as may be anticipated in the future, this will certainly be the preferred raw material. Lowered acetylene cost will lower the cost and increase the utilization of all of the members of the versatile vinyl acetate family of polymers, because each will become more competitive with the other products in its specialized markets.

#### ACRYLONITRILE

Acrylonitrile is an interesting example of the opportunity of choice of raw materials and processing in making a given product. Here, the classic production from acetylene and hydrogen cyanide has been largely upset, not because of the high price of acetylene, but because of the new processing techniques based on the synthesis of acrylonitrile from ammonia and propylene gas. Processes have been developed by Standard Oil of Ohio and DuPont in the United States of America; Distillers Company in the United Kingdom; Asahi Chemical Company in Japan; and others. However, with acetylene at a lower cost, it may be expected that the trend may be reversed, particularly in view of the cost of licensing and engineering the plants based on propylene, and the improved processes which have been developed for making hydrogen cyanide. Furthermore, as the demand has been growing in recent years, acetylene at less than 5 cents might even considerably increase the over-all market for the material, which now sells for about 15 cents per pound.

#### OTHERS

Trichloroethylene may be made from either ethylene or acetylene; oxy-chlorination will certainly take over the production of trichloroethylene unless acetylene at a lowered cost then that long maintained is available for large-scale petrochemical utilization.

Some specialties may be made much more readily only from acetylene, and others most conveniently from ethylene; and there is thus no competition between the two gases. However, the development of many of the acetylene derivatives of higher molecular weight has been seriously hampered by acetylene at 10 cents per pound, and cutting this to one-half or one third-will greatly increase the markets.

Increasing fuel uses with low-cost acetylene is to be expected; and in some places, lighting and cooking fuel may well be supplied by acetylene in tanks, either pure or directly from a reactor, mixed with hydrogen, in those places where liquefied petroleum gases are not available.

## CONCLUSIONS

The lowered costs of acetylene that may be expected from the development of improved processes for its production from natural gas or petroleum liquids will markedly increase its productive use. The optimum process - and this seems to be close to commercial realization - is one which would have almost a 100 per cent conversion of a hydrocarbon on a carbon basis in a single pass to acetylene. The gas stream should consist substantially only of acetylene and hydrogen. The cost of the acetylene so produced should be in the range of 3 to 5 cents per pound --- the lower figure if the hydrogen produced simultaneously is valued at its normal price as a chemical raw material; the higher figure if the hydrogen is valued only as a fuel. Substantial progress has been made in achieving this low-cost process, which should be available for commercial installations within the next two years.

Particularly the simpler and less expensive plants which should produce acetylene in such an optimum process will have low capital charges and will speed petrochemical production because of the relatively simpler and more economic chemical processing usually associated with acetylene as compared with ethylene in making intermediates and monomers for further processing.

This should be especially noteworthy in planning petrochemical production in developing countries, where the basic materials must be made available cheaply in relatively small plants, the production of intermediates and of final consumer products, and the markets for these products must all be developed simultaneously. Acetylene made from imported calcium carbide allows entrance into this sequence midway, and with lower cost processing for the ultimate products. With some markets established, the raw material — acetylene may then be developed locally from hydrocarbons. Thus, a reasonable programme over some years may be considered, rather than the building of a whole series of plants to produce consumer products for which the markets must also be developed.

On the other hand, olefins as by-products from cracking operations for gasoline will be major contenders as raw materials, particularly for very large-scale operations. However, plant and processing for chemical production therefrom, will be relatively more expensive and more complicated than from acetylene.

## **13. AROMATICS: BETTER TO IMPORT OR TO PRODUCE?**

## J. W. Andrews and R. E. Conser, Universal Oil Products Company, United States of America

In the course of building a petrochemical industry, a developing country must consider the point at which it will be economical to install facilities for the production of aromatic hydrocarbons. Aromatics are a basic intermediate in the production of a wide variety of chemicals; listed below are some of the important chemicals derived from certain of the most commonly available aromatics.

Benzene. Styrene, phenol, dodecylbenzene, cyclohexane for caprolactam, hexachlorobenzene, etc.;

Toluene. Trinitrotoluene, tolylene diisocyanate for polyurethanes, phenol, benzoic acid, caprolactam;

C. Aromatics. Para-xylene — terephthalic acid for polyesters, ortho-xyk ne — phthalic anhydride, ethylbenzene — styrene, meta-xylene — isophthalic acid.

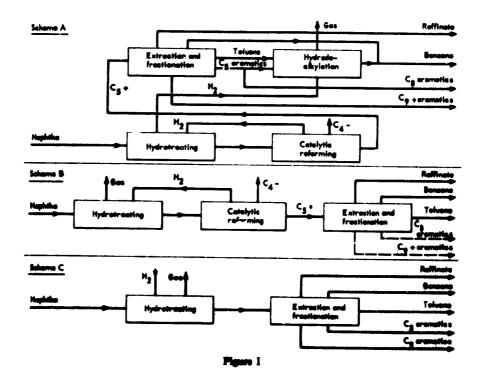
Until approximately ten years ago in the United States of America, and less than five years ago in Europe, coke-ovens were by far the predominant source of chemical aromatics. However, with the advent of Platforming <sup>(B)1</sup> catalytic reforming in 1949, and Udex<sup>1</sup> extraction using glycols in 1952, significant quantities of high-purity aromatics could be derived at relatively low cost from petroleum. As the supply of aromatics from coke-oven sources has become inadequate to meet the rapidly growing demand for these materials, production from petroleum has been widely accepted.

The production of aromatics from petroleum is highly capital-intensive --- i.e., a large capital investment is required per unit of production and economics of scale are important --- therefore, a developing country considering the installation of aromatics production facilities must carefully calculate whether or not the foreignexchange savings and continuity of supply are offset by higher production costs associated with a small-scale unit. To indicate the more important factors that must be taken into account, this paper will discuss the following: production costs as a function of size, complexity of the aromatics production facilities, feedstock and byproduct values; yields of aromatic hydrocarbons from different naphthas available in developing areas; and the magnitude of freight costs for shipping aromatics from industrialized countries in relation to over-all

<sup>1</sup> Trademark.

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productions costs. The effect of these factors apparently varies considerably from area to area, judging by the size of recent installations for aromatics production. Several are in the range of 10,000-50,000 tons per year of total aromatics, while some installations planned for the near future will produce several hundreds of thousands of tons of aromatics annually.

Before examining economic factors, a brief description of flow schemes for aromatics production would be appropriate. Figure I shows three flow schemes:

Scheme A will be considered in detail in this study; Scheme B will be briefly evaluated; and

Scheme C is included simply as an illustration of a possible additional source of petroleum aromatics.

In Scheme A, a  $C_6$ - $C_8$  petroleum fraction is charged to a hydrotreating unit for destruction of sulfur-, nitroger-, and oxygen-containing compounds. The purified naphtha is then charged to a Platforming unit, in which the most important reactions for aromatics production are the dehydrogenation of naphthenes and the dehydrocyclization of paraffins. The catalytic reformate is fed to an extraction unit for recovery of benzene, toluene, and  $C_8$  aromatics. Excess toluene and  $C_8$  aromatics are converted to benzene in a hydrodealkylation unit.

Scheme B is similar to Scheme A, except that the hydrodealkylation unit is eliminated. Therefore, Scheme B operation feedstock will yield a much larger proportion of toluene and  $C_0$  aromatics than will Scheme A. This Scheme will be economically appealing when the benzene and other aromatics that can be produced without hydrodealkylation are in the proportions required to meet projected market demand. However, benzene is the

aromatic most usually in greatest demand and to produce a maximum of this material using Scheme B a narrower naphtha cut is used as feed.

Scheme C is a method of recovering pure aromatics from by-product gasolene resulting from olefin production operations, and requires only a hydrotreating and an extraction step. Hydrogen availability and cost play an important part in the economics of this Scheme, owing to the large quantity of hydrogen required to saturate diolefins and olefins in the by-product gasolene.

The potential yields of benzene, toluene and  $C_0$  aromatics from the  $C_0$ - $C_0$  portions of several common naphthas are shown in table 1. These yields are indicative of the level of aromatics that can be obtained from the various charge stocks, but are by no means optimized to any specific economic situation.

The five naphthas were chosen to represent a wide variety of cyclic contents in the feeds, which cyclics determine aromatic yields to a large extent. The naphtha stocks are arranged in ascending order of cyclic content. from Kuwait/Arabian to Oficina. Nigerian and some Indian naphthas are even richer in cyclic hydrocarbons than the stocks shown. The yield of hydrogen, which is important in determining the amount of alkylbenzenes that may be converted to benzene, is also shown. It will be noted that this yield depends not only upon the actual content of naphthenes present but also upon the proportion of naphthenes to aromatics in the feed. Over-all yields according to the processing sequence Scheme A of figure 1 are shown; all of the toluene and as much as possible of the C<sub>0</sub> aromatics are converted to benzene using the hydrogen produced by catalytic reformine.

	Broatt/	Agha Juri	The Juana	Libyan	Officina
Produceck					
Distillation, C	65-145	65-145	65-145	65-145	65-145
Wt-% on grude	10.5	12.5	6.0	14.0	14.0
Specific gravity	0.728	0.738	0.735	0.737	0.761
Hydroserbon types					
Parallas, w%	68	60	55	50	40
Naphthenes, wt-%.	20	25	34	46	38
Aromatica, wt-%	12	15	11	4	22
Catalytic reforming yields					
Hydregen, wi-%	1.30	1.44	1.71	2.16	1.66
Hydrogen, m <sup>4</sup> /t.	145	160	190	240	185
Dennene, wt-%	4.3	5.9	6.6	4.6	6.2
Toluene, wt-%	13.8	13.5	16.8	17.6	21.2
C. aromatias, wt-%	19.6	21.9	19.7	21.3	22.5
Co+ aromatics, w1-%	5.4	7.1	7.6	10.3	8.4
Yloids, w-%					
	22.9	26.2	32.0	35.2	33.9
C <sub>p</sub> aromatica	- GJ	5.7			4.3
C_*erometics.	40	5.3	5.7	1.5	6.3
C <sub>a</sub> +rafinete	37.8	34.1	34.8	33.2	30.8
C and lighter games	20	28.7	27.5	30.1	24.7

TABLE 1. ESTIMATED PERDETOCK PROPERTIES AND YIELDS

The economics of producing aromatics vary significantly according to the cyclic content of the feed. Lower cyclic contents result in higher feed capacities for the same level of aromatics production and require more severe operations in the catalytic reforming unit in order to achieve a significant level of aromatics production. For investigating the variation of economics with plant size (so-called "economics of scale") Apha Jari naphtha, which is intermediate in cyclic content has been selected for study. Here again, however, the yields have not been optimized to the assumed price structure. Our economics will be based upon operations of the particular proprietary process units with which we are familar, i.e., Unifining (hydrotreating). UOP Platforming (catalytic reforming), Sulfolane" (aromatics extraction) and Hydeai (\*)" (hydrodealkylation). The following assumptions are made:

- 1. Installation in an existing refinery, with availability of existing offsite facilities;
- 2. Air cooling with allowance for trim water cooling, and electric drives on pumps and compressors;
- 3. Straight-line depreciation over ten years, with no salvage value;
- 4. Borrowed capital at an interest rate of 6 per cent on the unpaid balance, with repayment in equal installments over ten years;
- 5. Naphtha feed, railinate from the extraction unit and  $C_0 +$  aromatics valued at \$20 per ton;
- 6. Fifteen per cent desired annual rate of return on investment, with a project life of ten years.

In working from the naphtha value to aromatics cost, discounted cash flow is used to account for this 5 per cent return on investment. This concept, which is now widely used for the evaluation of projects in the petroleum and chemical industry, may be compared with an ansuity. Thus, an initial outlay is made; this outlay to be roturned over a period of years along with "cash flow" at a given rate on the unpaid balance. The high required rate of return of 5 per cent for this project reflects the risks inherent in such an investment owing to the possibilities of technological obsolescence of the process, later installation of a unit with more favourable comomics of scale, change in markets, change in position of the company, or loss of production due to damage to the unit. However, these risks are less for an aromatics production unit than for other types of chemical plants, since bearers is an important basic intermediate and the technology of aromatics production is well developed.

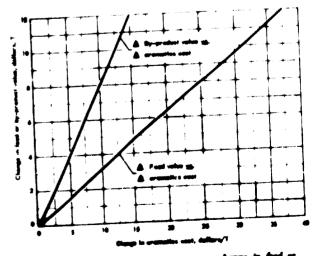
Beomomics are presented for the processing of Agen-Jeri naphthe by both Scheme A and Scheme B as shown in figure 1. Estimated yields and utility requirements are shown in table 2 for the processing of an Agen Jeri Cr-Ce naphthe by Scheme A and essentially a Ce fraction by Scheme B. The Scheme A operation includes hydrodealitylation of all of the toluone and as much of the Ce arometics as is possible with the available hydrogen. The superity of the complex has been set at 30,000 tess of obsenies arometics assessably. The Scheme A total instudes beness and xylenes in the ratio of about 5:1, assuming

TABLE 2. ESTMATED YELDS AND UTILITY REQUIREMENTS Aske Jarl Rephrite

والمرجوع المراجع المراجع المراجع المراجع المراجع المراجع المراجع المراجع المراجع المراجع المراجع المراجع المراجع	Scheme A	science B
Feed, tons annum	94,000	152,000
Products, tons/annum. Bonzone	24,650	10,0 <b>0</b> 0 10,000
Toluene C <sub>a</sub> aromatics C <sub>b</sub> - aromatics C <sub>b</sub> - railmate C <sub>b</sub> and lighter gases	5,350 5,000 32,000 27,000	100,000 12,000
Estimated attitutes Fuel, 19 <sup>a</sup> kcal/hr Cooling water, m <sup>a</sup> /hr. Power, kWh	23 130 1,279	24 109 1,079

that it is desired to recover para-xylene or ortho-xylene for further processing and thus giving the xylenes chemical value. C<sub>0</sub> aromatics are assigned a nominal byproduct value for Scheme B, it is assumed that only beams is required, and the by-product toluene is given a nominal by-product value. If these by-product aromatics could be sold as solvests, say, or if the raffinate (about 86 F-1 octane with 3 ml TEL) could be used for motor fuel blending, the economics would be improved as shown in figure 11.

Table 3 summarizes estimated investment costs. These costs were taken from our generalized correlations, which are based on Gulf Coast, United States of America, erection. The allowance for storage includes three weeks' product storage plus sufficient intermediate storage for regeneration of the Platforming and Hydeal units. Estimated total investment costs (excluding working capital) are plotted against aromatics capacity for the Scheme A operation in figure III; the Scheme B figure for



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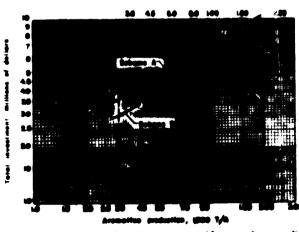
TABLE 3. ESTIMATED INVESTMENT

	Scheme A B	Scheme B B
Unifining and Platforming units Suifolens and aromatics fractions-	<b>980,68</b> 0	1,1 <b>90,0</b> 90
tion	950,000	900,000
Hydeai unit and feed H <sub>s</sub> cleanup	800,000	
heaverial and Labour subtosal	2,650,000	1,950,000
Design, engineering and contrac- tor's charges	538,678	480,890
Process proched pool	3,208,000	2,350,000
intermediate and product storage	330,889	450,000
laitial outalysts and chemicals	170,000	230,060
TOTAL INVERTMENT	3,720,000	3,030,000
Working capital allowance	466,669	458,688

production of 30,000 annual tons of bonzone is also shown on this graph.

The calculation of direct operating costs is shown in table 4. The assumed on-stream efficiency is 330 stream days per annum, or 90 per cent.

Table 5 shows the back-calculation of the cost of producing aromatics in order to achieve the desired 15 per cost rate of return. The cash flow required is based on achieving a 15 per cost rate of return over ten years on the unpaid balance of the total investment plus working capital, assuming a residual or "salvage" value equivalent to the working capital. From this each flow is subtracted association to arrive at an after-tax profit figure. An assumed tax rate of 50 per cost is used to determine the before-tax profit. Operating expanses are added and by-product credits subtracted to arrive at the aromatics cost. This figure is divided by 30,000 annual tens to arrive at a cost per ton.



Pigere III. Parlation of Intel Investment with cremellar experits

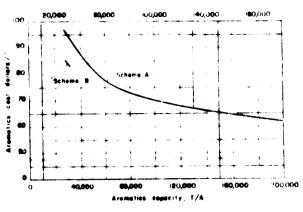


Figure IV. Variation of aromatics cost with capacity

Figure IV shows the variation of aromatics cost with aromatics capacity for the Scheme A operation. The Scheme B figure, representing a production of 30,000 tons per year of benzone without hydrodealkylation, is plotted for comparison. Note that a capacity of about 45,000 tons per annum of aromatics for a Scheme A operation is required to achieve the Scheme B aromatics cost level at a 30,000 tons per annum production rate. Doubling of the Scheme A aromatics capacity results in nearly a 20 per cent drop in production costs.

The variation in aromatics production costs with naphtha feed value and by-product value is shown in

## TABLE 4. CALCULATION OF DIRECT OFFRATING COUTS

330 stream days annum

		calandar das
Unit value		Schemer B
Labour		
Operating labour. 51.50/hr Supervision	216 43	144 29
	259	173
Laboratory Estimated at.	49	30
Untitates		
Puol S1.30/10 <sup>4</sup> kon Cooling water S8.004/m <sup>2</sup>	L 749 11	847 9
Power S0.01/LWb	276	232
	1,896	1,000
Chundenie Catalysts and sufferance	100	250
Nåndnatomation Turkunstand och 2 M/100		
Balanced at 3 %/en- mus of process in- verticent	263	198
Tuens, separat artitude.	1,776	1,794

TABLE 5. CALCULATION OF ABOMATICS VALUE (In thousands of US dollars per annum

	Scheme A	Scheme #
1. Cash flow required for 15 per cent	<b>80</b> 1	672
2. Amortization on investment	372	303
3. Profit required (1-2)	429	369
4. Income taxes, 50 per cent of pre-tax profit	429	369
5. Pro-tax profit (3 + +)	858	736
6. Total operating expenses Feedbtock or \$20/t	1,800	3 <b>,040</b>
Direct operating costs (table 4)	649	633 160
Allowance for overhead Taxes and insurance, 2-1/2 per cent of equipment. Amortization, 10 per cent of total in-	160 <b>39</b>	70
Vestment	372	303
Interest, 6 per cent on unpaid balance	136	118
TOTAL OPERATING EXPENSES	3,226	4,264
7. Required totat revenues (5 + 6)	4,994	5,002
8. By-product credits at \$20/t	(749)	(2,200)
9. Fuel gas produced at \$1.50/10 <sup>4</sup> keal	(500)	(275)
19. Product cost (7-8-9)	2,844	1,527
PROPUCT CONT/L	<b>995</b>	384

figure 4. Use of the by-products for motor fuel blonding or as specialty products, with consequent substantial changes in value, would affect aromatics production economics considerably. The effect of feedstock value is particularly interesting, however. An aromatics producer, employing a Scheme A operation at a production level of 30,000 tons per year, could compete with a producer nearly twice as large if his feed nephtha were 35 per ten cheaper, other economic considerations being equal.

The cost of transporting aromatios can be quite significant when compared with production costs. Owing to its low flash point and toxic properties, beasene is quite

expensive to transport. For instance, the single-charter rate for shipping benzene from a northern European port to Middle Eastern ports has been quoted at \$35 to \$70 per ton. If transportation to an inland destination is added, the total transportation costs could exceed production costs. A higher flash-point material, such as mixed C<sub>g</sub> aromatics or products of the further processing of benzene, could be shipped at half the above rates or less, and lower rates could be obtained under a long-term charter. Nevertheless, it is clear that a small aromatics plant serving a local chemical industry would have considerable protection through transportation costs from large aromatics plants located at a distance.

These economic calculations do not take into account the possibility that, during a period of over-capacity, aromatics might be shipped from an industrialized area at a price not providing full return on investment, but simply covering direct costs and a portion of overhead. Such a situation should not be permanent, however, since erection of new units during this period of overcapacity would slow down considerably until domand increased to such a relation with capacity that prices would return to a level sufficient to yield an economic profit.

A study of this type caanot take into account all factors that could apply in an individual case, such as: reduced initial throughput or distress sale of aromatics to a neighbouring area, the desirability of conserving foreign exchange, tariffs, respresal trade arrangements and differences in construction costs between countries.

Some general conclusions may be drawn, however:

- 1. Acomatics yields and concomitant economies can very widely depending upon the nephtha source;
- 2. Plant espacity has a very significant effect on aromatics production costs, particularly in the region of aromatics espacities that a developing country would with to consider:
- 3. Lower food nephths prices and freight costs can offset the economic effects of a large difference in plant capacities; when balance of payments and reliability of supply are also taken into account, the installation of a smaller-scale aromatics plant in a developing country is a worth-while consideration.

## 14. BENZENE BY HYDRODEALKYLATION USING THE DETOL PROCESS

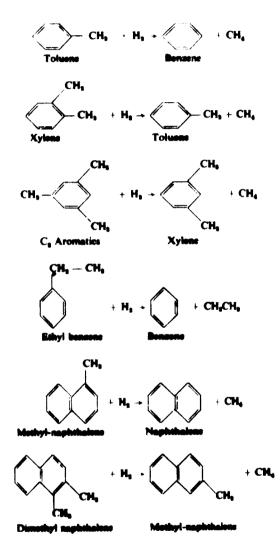
R. G. Craig, L. C. Doolp, A. K. Logwinsh, Houdry Process and Chemical Company, Division of Air Products and Chemicale, Inc., United States of America

Arometics production from petroleum should be considered in the development of any chemical industry Of the various aromatics which may be considered. bensone, tobuone, xylone and naphthalone are of principal importance. Benzens, the simplest substance of aromatic chemistry, was first obtained in commercial quantities by dry distillation of coal. For many years the ooking of coal was not only the main supplier of these aromatics but also in fact the only source. As the domand for the monocyclic aromatics increased, it was covered from petroleum sources. Degianing about 1950, beasene was produced commercially from petroleum. Catalytic reforming of naphthas increased the yield of bearene, toluene, ethyl benzene and xylence by dehydrogenation and isomerization of naphthenes. Yields of tobsens and xylenes from petroleum exceeded that of beamene and in fact encouded the chemical market domand. Concequently, even though the growth of reforming for aromatic production has been phenomenal, it has not been able to meet the growing need for bennene in many areas. To alloviate the deficiency, a number of dealkylation procomes which permit conversion of toluene and xylenes to bunness have been developed. Some of these processes also offer the possibility of converting alkyl naphthalenes to naphthalene. The Houdry DETOL process is one of the commercially proved dealkylation processes (1).

Before discussing the DETOL process, it may be of interest to note briefly the end uses of benzene. The largest quantities are used for the production of styrene and phenol. Nylon is the next largest consumer of benzene whether made via the adipic acid or the caprelactam routes. Lesser and users, but users of significant importance, are detorgents, insecticides such as hensehlorebenzene and DDT, malsic anhydride, aniline, chlorinsted benzenes, mitrobenzene, etc. Thus, for a developing country, benzene is of prime importance as the starting material for the manufacture of plasting, fibres, detergents, insecticides and polyesters.

#### Description of DESOL process

The principal feature of the Houdry Durot, process is the estabytic dualkylation of generally available refinery aromatic streams to produce specific, high-gende prometic chemicals. As the result of selective dealkylation, pure aromatic products of lower earbon number are obtained. The Durot, process is specifically designed to earry out the following reactions individually or collectively.



When the arometic contains more than one alkyl side chain group, consecutive dealkylation takes place. For example, a C<sub>0</sub> arometic such as mositylone is first dealkylated to raste-sylene, then toluone and finally benaese. Similarly, d'unthyl-naphthalene is consecutively dealkylated to setthyl-naphthalene and nephthalene. The kinetics of these dealkylation reactions with the Houdry Dates, establish here been shown to fit 1.5 order expressions (2) (3). The reaction is first order with respect to hydrocarbon concentration and 0.5 order with respect to hydrogen concentration,

r = rate of dealkylation k (hydrocarbon) <sup>1.0</sup> (H<sub>3</sub>) <sup>0.5</sup>

where hydrocarbon and hydrogen concentrations are in molar units. Although it has been shown that the above reaction occurs thermally according to the same rate equation, it has also been shown that the activation energy for the Houdry DBTOL catalyst is 35 kcal/gram mole compared with a value of  $50 \pm$  kcal/gram mole for the thermal reaction. Thus, at the same temperature, the rate of reaction for the DETOL catalyst is more than an order of magnitude greater than the thermal reaction rate. Since the DBTOL process can utilize lower temperatures to achieve higher conversions per pass, dealkylation selectivities are higher than those for thermal reactions. As an example, benzene selectivities of 96+ mole per cent for toluene dcalkylation have been consistently obtained in commercial operation.

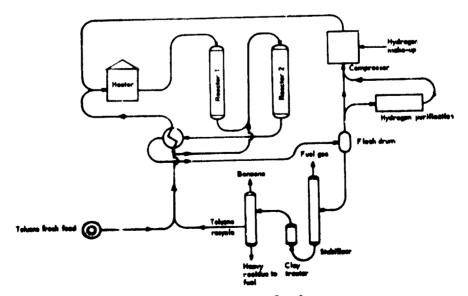
From the standpoint of hydrogen consumption, it is desirable to process feedstocks that are 100 per cent aromatic. Since most charge stocks contain minor quantities c' sulfur compounds, paraffins, naphthenes and olefin, the DETOL process must remove these by secondary reaction. Sulphur compounds such as thiophenes and mercaptans are completely converted to H<sub>s</sub>S and aliphatics. Paraffins, olefins and naphthenes are hydrocracked to Cs and lighter hydrocarbons, which are easily separated from the gromatic products. The two major sources of non-selectivity result from the hydrogenation and condensation of aromatic rings. To a very limited extent, aromatic nuclei are hydrogenated to cyclohexane homologues. This reaction, however, is suppressed by the relative inactivity of the catalyst for ring hydrogenation and the very unfavourable thermodynamic driving force for this reaction. The quantity of cyclohexane found in product benzene typically ranges

from 0.01 to 0.05 mole per cent. A second non-selective reaction is the condensation of aromatic nuclei to produce byphenyl, methyl-byphenyl, bybenzyl, fluorene and anthracene. In general, the production of these compounds is minimized by the relatively lower temperature level employed in the catalytic process. Production selectivities are generally quoted on a once-through basis, in which cases there is a net condensed ring production. However, the ultimate selectivity can be increased above this value if condensed rings are re-circulated to extinction.

Figure 1 shows a typical process flow diagram for a toluene to benzene dealkylation plant. Toluene fresh feed is exchanged with reactor effluent and finally brought to reaction temperature along with recycle and make-up hydrogen in a fired preheater. The combined feed then flows to two DETOL reactors in series.

Since dealkylation reactions are highly exothermic, a slip stream of liquid aromatics feed is injected between the first and second reactors to adsorb the heat of dealkylation in the first reactor. The effluent from the second reactor is cooled, condensed and separated. The flash drum liquid is fed into a stabilizer, where the light hydrocarbons and dissolved hydrogen are taken overhead. The bottoms from the stabilizer are fed through a fixed bed clay treater. For many benzene uses, clay treating is not required since the bromine index (bromine number multiplied by 1,000) of the stabilized product is quite low (below 200). The clay-treated aromatic liquid, or the stabilizer bottoms, is then charged to a benzene fractionator, where high purity benzene is taken overhead. Unconverted aromatics are recycled to the process. Heavy residue rejected from the benzene fractionator is taken to fuel.

Most of the overhead from the high-pressure flash drum is recycled to the process. A portion of this stream may be passed through a hydrogen purification unit to maintain an optimum hydrogen purity in the process. Fresh hydrogen is fed to the unit from any suitable



Planto I. Datal. process flow sheet

source such as catalytic reformers or steam methane generators. Typical operating conditions for the DETOL reactor section are as follows:

	English	Metric
Femperalure	1,000-1,200°F 500-1,000 psig	540-650°C 35-70 kg/cm <sup>2</sup> ga

The DETOL catalyst is extremely stable and rugged. Under the conditions of the process, coking does take place at a very low rate, requiring reactor inlet temperatures to be increased gradually over a period of about six months. The catalyst, however, is easily regenerated by conventional means and restored to its initial activity and selectivity. The ultimate catalyst life in the DETOL process is not known. As of this writing, the first DETOL unit to go on stream in 1961 is still using the original charge of catalyst.

#### Benzene purity

Benzene produced by catalytic hydrodealkylation is the purest commercially available. Typical inspections from commercial operation show 99.95 per cent benzene, freezing point well over 5.4°C., thiophene of less than one part per million (typically 0.2 ppm) and non-aromatics of 0.01 to 0.05 mole per cent. These values are superior to those for petroleum benzene produced by extraction.

Because of the availability, at very high purity, of petroleum benzene and benzene from hydrodealkylation, rigid quality specifications have been established irrespective of the need for high quality in some chemical reactions. These specifications cannot be met by normal coke oven by-product aromatics. To compete with petroleum aromatics the coke oven operators in the United States of America have had to upgrade their aromatic by-products. However, severe treatment with the conventional sulfuric acid methods, the most commonly used process, results in increased expense and high aromatic losses but still does not ensure a quality product unless aliphatics are absent or are removed by some other means. The solution to the problem of United States coke oven operators was found in the single step multifunctional catalytic LIDE process which desulfurizes, hydrocracks non-aromatics, and dealkylates alkyl benzenes to benzene, producing a high-purity benzene comparable to that obtained from petroleum extraction or hydrodealkylation. As the impact of petroleum benzene increases in other areas of the world; similar problems will develop.

Although our objective is to discuss the DETOL process and to consider its accompanying economics, the LITOL process is mentioned because some developing countries contemplating a steel industry may very well find it necessary or desirable to upgrade coke oven aromatics.

#### DETOL process yields

Process yields are summarized in tables 1, 2 and 3. These tables show respectively the effects of variations in make-up gas purity, make-up gas quantity, and aromatic feed composition to the reactors. In general, the molar yield of benzene is unaffected by changes in these factors. However, they are quite important in process economics to be presented later.

Actually, it is possible to operate the process at higher or lower net yields of benzene from the feed aromatics (higher or lower selectivity). This is accomplished by changing the severity of operation through control of the

TABLE	1.	HOUDRY	Dete	ol pri	DC ESS	<b>-</b> ·	MATERIAL	BALANCES
		<b>BPFBC</b>	TOP	MAK	- <b>/P</b> G/	<b>IS P</b>	JRITY	

Moles/100 moles fresh fered

Can		)	)			2			4			
Maheup gas pu	rity, vol. per	cent	5:	53		53 80		)	1	5	None	
	Prest. Joed	Bonz. prod.	Make-up gas	Puels prod.	idako-up yar	Puole prod.	Mako-up pue	Puela prod.	Make-up gas	Fueir prod.		
Componente												
Н			132.1	26.0	136.0	29.8	129.1	23.0		36.2		
C <sub>1</sub>			57.5	156.3	31.4	130.5	6.8	105.8		30.5		
<b>G</b>			27.7	30.6	2.6	5.5		3.0		1.5		
G			22.2	23.0		0.8		0.8	-	0.6		
<b>C</b>			10.0	10.0					Ž			
Benzene	0.7	96.8		0.1		0.1		0.1	Ź	0.1		
Tokuene.	98.9	0.1										
Eth. benzene .	0.3											
o-Xylene												
m-Xylene	0.1											
p-Xylene												
Diphenyt .				0.8		0.8		0.8		0.8		
TOTAL	100.0	96.9	249.5	246.8	170.0	167.5	135.9	133.5		79.7		

## TABLE 2. HOUDRY Detai PROCESS --- MATERIAL BALANCES REFECT OF VARYING THE MAKE-UP GAS QUANTITY

	2				1	,	
c 11	28	21	0	22	10	30	J
	Fuels prod.	Make-np gas	Puole prol.	Make-up sas	Fuels prod.	Make-up gas	Puelo prod.
136.0 31.4 2.6	29.8 130.5 5.5	232.5 53.9 4.4	126.9 152.9 7.3	232.5 53.9 4.4	126.9 152.9 7.5 0.8	323.5 74.8 6.1	217.5 173.7 9.1 0.8
	nz. Make-up par 136.0 31.4	nz. Make-up Puels nd. pas prod. 136.0 29.8 31.4 130.5 2.6 5.5	lc 128 22 tr. Make-up Puels Make-up tr. Make-up prod. and 136.0 29.8 232.5 31.4 130.5 53.9 2.6 5.5 4.4	nz. Make-up Puol: Make-up Puol: d. pool. and prod. and prod. 136.0 29.8 232.5 126.9 31.4 130.5 53.9 152.9 2.6 5.5 4.4 7.3	2 3 220 22 128 220 22 128 8as prof. Make-up Puels Make-up puel 136.0 29.8 232.5 126.9 232.5 31.4 130.5 53.9 152.9 53.9 2.6 5.5 4.4 7.3 4.4	Ic         136         230         220           It         Make-up prof.         Make-up prof.         Make-up prof.         Make-up prof.           136.0         29.8         232.5         126.9         232.5         126.9           31.4         130.5         53.9         152.9         53.9         152.9	2         3         220         230         30           ic         138         220         230         30           is:         Make-up prof.         Paols         Make-up prof.         Paols         Make-up prof.         Make-up pr

290.8

0.3

TR

0.8

289.0

290.8

Moles/100 moles fresh feed

0.1

0.8

167.5

170.0

operating temperature or residence time. However, increases in severity are accompanied by non-linear decreases in selectivity and increases in plant investment or in catalyst inventory.

96.8

0.1

96.9

0.7

98.9

0.3

0.1

100.0

Make-up pi

Componente

H. . .

**C**<sub>1</sub> . .

С,,.

Name

Toluene Eth. Bonzone

o-Xylene

m-Xylene p-Xylene

Diphenyl

ŝ

ŧ

TOTAL

C, .

A decrease in severity does result in improved selectivity. However, this improvement is gradual, with decreasing severity since the normal selectivity of 97 molar per cent leaves little room for improvement. Furthermore, the increased total feed rate which results from lower conversion and higher aromatics recycle requires additional utilities consumption and plant investment.

All data in tables 1 and 3 and cases 2 and 5 of table 2 include purification of the hydrogen-rich recycle gas stream. With the exception of case 5, these all represent plant operation with minimum hydrogen-rich make-up gas. The minimum make-up gas contains approximately 120 per cent of the stoichiometric hydrogen requirement in order to allow for hydrogen losses in the liquid product from the high pressure gas-liquid separation, hydrogen losses with the reject light hydrocarbons from the recycle gas purification unit and hydrogen vented to control plant pressure. Case 5 shows the effect of increased

0.4

0.8

289.3

404.4

TR

0.5

0.1

0.8

402.5

TABLE 3. HOUDRY Detel PROCESS --- MATERIAL BALANCES SPEECT OF FEED COMPOSITION

Moles/100 moles fresh feed

constant benzene production, minimum make-up gas

				9			
Case	Bone. prod.	Presh feed	Maho-up gao	Paola prod.	Presh food	Maho-no gar	Paste prof.
Components							
-			127.5	21.3		173.1	26.8
<b>Н</b> <sub>1</sub>			29.4	128.5		40.1	174.0
<b>G</b>			2.4	5.3		3.3	11.8
<b>G</b>				0.8			0.8
<b>C</b> <sub>1</sub>				0.1	0.4		TR
	96.3	0.7		A.1	53.5		•
	0.1	96.9			33.3 <b>5.9</b>		
Eth. Benzene		0.3					
e-Xylane					11.2		
m-Xylene		6.1			28.1		
p-Xylene					8.9		
Diphonyl				0.8			
TOTAL	96.9	100.0	199.3	156.8	108.0	216.5	214.1

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Mathem         Mathematication         Mathmatimatication         Mathematication											
		8	8	8	1	121	ភ	â	8	Tolmer	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		-			•		2	•	4	•	•
Matrix Matrix		-									•
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		•	•	•	•	•	•	•	•		•
Open matrix         1,215,500         1,215,500         1,215,500         1,215,500         1,215,500         1,215,500         1,215,500         365,000         365,	Made up put compressor	115,000	000'001	85,080		100,000	150,000	150,000	195,000		1.260.000
Dynamical fragment         MX, Marce		1,235,000	1,215,000	1,215,000	1,215,000	000,012,1	<b>000</b> CI7'I				
Dynamic interview         410,000         355,000         1,075,000         300,000         300,000         1,990,000         <	Ony treater and fraction-		345,000	365,000	365,000	365,000	365,000	345,000	365,000	365,000	365,000
Total         2,700,00         2,000,000         2,000,000         2,000,000         2,000,000         2,000,000         2,000,000         1,000,000         1,000,000         1,000,000         1,000,000         2,000,00         2,000,00         2,00	Cynese H, paris		410.000	000,205	000'5/0'1	410,000	340,000	I	1	420,000	470,000
<i>I.S. consper U.S. public barrane product</i> <b>XXVII Upp</b> (1.200)         (1	1	1210,000	2,076,000	2,050,060	2,655,000	2,090,000	2,070,000	1,920,000	1,795,000	2,100,000	2,215,000
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $					U.S. cents per l	J.S. <b>ga</b> llon benze	ne product				
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $											
			(91876)	(01976)	(19070)	(968.0)	(1.280)	(1.228)	(1.620)	(0.865)	(997.1)
		Į	0.905	1.530	1	0.906	1.545	1.545	101.2	0.640	1.12
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		ā	0.168	0.154	0.1%	0.168	102.0	212.0	767-0	0.105	641.0
W/1 (000 h)         0.175         0.170         0.165         0.165         0.165         0.165         0.165         0.165         0.165         0.165         0.165         0.165         0.165         0.165         0.165         0.165         0.165         0.165         0.165         0.165         0.165         0.161	Casting week, 24/1,000	1		0112	0.130	0.114	0.110	0.121	0.108	0.115	0.122
K.M.         0.536         0.462         1.273         0.513         0.462         0.741           C.M.         0.113         0.165         0.165         0.166         0.166         0.166         0.166           C.M.         0.113         0.165         0.166         0.166         0.166         0.009         0.009           C.M.         0.113         0.113         0.113         0.113         0.113         0.113           C.M.         0.000         0.000         0.000         0.000         0.000         0.000         0.000           M.M.         0.113         0.113         0.113         0.113         0.113         0.113           M.M.         0.294         0.394         0.394         0.394         0.394         0.394           M.M.         0.294         0.249         0.244         0.244         0.244         0.244           M.M.         0.299         0.603         0.603         0.603         0.603         0.603           M.M.         0.244         0.244         0.244         0.244         0.244         0.244           M.M.         0.613         0.613         0.613         0.613         0.613         0.613      <	•	12		0.167	0.248	0.170	0.165	0.158	0.158	0.159	0.185
K + 4         0.356         0.42         1.13         0.115         0.165         0.164         0.213         0.214         0.213         0.214         0.213         0.213         0.214         0.213         0.213         0.214         0.213         0.214         0.213         0.214         0.213         0.214         0.213         0.214         0.213         0.214         0.214         0.213         0.214         0.214         0.213         0.214									1.035	0.417	0.369
Columnation         0.173         0.165         0.164         0.165         0.164         0.213           Columnation         0.000	Sub-true	0.536	0.467								
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		ļ		21.0	1710	9165	0 164	0.213	0.174	0.166	0.215
GLI23         GLI34         GL133         G.173         G.173         G.173           GLI24         0.394         0.394         0.394         0.394         0.394         0.394           GLI25         0.394         0.394         0.394         0.394         0.394         0.394           GLI25         0.244         0.299         0.309         0.309         0.241         0.244           GLI3         0.259         0.663         0.663         0.603         0.636         0.636           GLI3         0.590         0.590         0.590         0.590         0.590         0.590         0.590           GLI3         0.590         0.590         0.590         0.590         0.590         0.590         0.590           M.         0.51         0.500         0.590         0.590         0.590         0.590         0.590         0.590           M.         0.51         0.511         0.613         0.511         0.590         0.590         0.590         0.590         0.590         0.590         0.590         0.590           M.         0.51         0.51         0.51         0.51         0.51         0.590         0.590         0.590		511 600	0.009	6000	0000	000'u	600.0	0.009	0.009	0.009	
Q         0.394         0.304         0.3								0.222	0.183	0.175	0.224
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	manime labour () man/					1			101.0	0 104	1010
(3 mode)         0.236         0.344         0.234         0.241         0.234           Series         0.653         0.633         0.613         0.613         0.613         0.241         0.236           Series         0.590         0.590         0.590         0.590         0.590         0.613         0.613           Model         0.590         0.590         0.590         0.590         0.590         0.590         0.590           Model         0.590		T.	<b>16</b> E.0	<b>16</b> 00	165.0	0.34	1.54				
Subserved         0.653         0.653         0.633         0.635         0.6455         0.775	agence (3 per cent of	748	10.244	0.239	0.309	0.244	0.241	0.224	0.209	0.245	0.258
Model         0.590         0.775 <th< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>0.618</td><td>0.603</td><td>0.639</td><td>0.652</td></th<>								0.618	0.603	0.639	0.652
M turne (1 per (15)Yr: st. line)         0.006         0.061         0.001         0.103         0.061         0.060         0.070           n(15)Yr: st. line)         0.573         0.541         0.531         0.6655         0.541         0.535         0.496           n(15)Yr: st. line)         0.775         0.775         0.775         0.775         0.475         0.496           n11.         0.775         0.775         0.775         0.775         0.775         0.775         0.775           St. total         1.967         1.976         2.153         1.967         1.980         0.775					0.590	0.590	0.590	0.590	0.590	0.590	0.590
(15)r.st. line)         0.573         0.541         0.531         0.665         0.541         0.535         0.496           1.         0.775         0.775         0.775         0.775         0.775         0.775         0.775           2.153         2.024         1.967         1.976         2.153         1.967         1.960	ad turns (1 per	ž	0.081		0,103	0.061	0.080	0.070	0,070	0,031	0.086
Paral:	<b>w.k</b> <b>m (15 yr. st. line)</b>	ST3	0.541	0.531	0.685	0.541	0.535	0.496	0.465	0.544	0.574
Sub-tener 2.024 1.967 1.976 2.153 1.967 1.980	pearl. administ	775	0.775	0.775	0.775	0.775	0.775	0.775	0.775	0.775	0.775
								1.931	1.900	066'1 (	2.025
Toria. (and. royally and feadmark 3.394 3.261 4.055 3.542 3.261 3.529 3.57		<b>1</b> 66.6						3.579	3.721	3.221	3.270

+ 254/MM RTU at 53 per cent hydrogen; 354/MM BTU at 80 per cent hydrogen; 1004/MM BTU at 95 per cent hydrogen.

make-up gas quantity. Case 4 shows recycle gas purification by hydrogen generation instead of cryogenic means.

Cases 6 and 7 depict operations without recycle gas purification. Case 6 represents plant operation with minimum hydrogen-rich make-up gas without recycle gas purification, and case 7 shows the effect of increased makeup gas quantity.

#### **Process economics**

The effects of make-up gas purity, make-up gas quantity with and without recycle gas purification and feedstock composition on process economics are shown in table 4 for plants producing 1,800 BPSD of benzene.

Considering first the effect of make-up gas purity, the use of low purity (low hydrogen content) or high purity (high hydrogen content) make-up gas results in higher processing costs than the use of 80 per cent hydrogen content make-up gas such as is normally available from catalytic reforming of naphtha to high octane gasolene. This would be expected for the low purity gas because provision must be made to purify it. However, this difference is small.

A larger processing cost differential exists if 95 per cent hydrogen is purchased and purification of the recycle gas by cryogenic means is also included. However, installation of a hydrogen generation plant to provide the required hydrogen and simultaneously purify the recycle gas results in a higher initial investment but a more attractive processing cost (case 4 of table IV).

Increasing make-up gas quantity at constant 80 per cent hydrogen purity is shown by cases 2, 5, 6 and 7 to result in reduced plant investment. However, processing costs increase with increasing make-up gas quantity and are, in fuct, higher by almost one-half a cent a gallon for the case with 305 per cent of the stoichiometric hydrogen than for the case with 128 per cent of stoichiometric hydrogen. This results from the particular economic structure assumed. Major differences in power cost and in make-up gas cost related to fuel value are apparent from consideration of table IV. These are only partially balanced by reduced capital charges. If make-up gas is available at fuel cost, the processing cost relationship is reversed even in spite of the compression costs involved.

Make-up gas was assumed available at 300 psig. Other pressures would affect both plant investment and compression (power) costs.

Another logical effect is shown by consideration of cases 8 and 9. Here the effect of processing aromatics

4

other than toluene is shown. Hydrogen consumption increases by the increase in alkyl groups (methyl and ethyl) which must be hydrogenated and make-up gas quantity increases accordingly. Fuel production also increases. The effects of these differences on benzene manufacturing costs arc small.

The cost of aromatic feedstock is by far the most significant cost in the production of benzene by hydrodealkylation. The effect of toluene price on finished benzene cost is shown below for an average processing cost of 3.3 cents per US gallon of benzene:

Toluene price ¢/gal									5	15	25
Tolucne cost ¢/gal. benzene									6.2	18.5	30.8
Processing cost ¢/gal. benzene .											
В	enz	cn	C	co	<b>s</b> 1	¢,	<b>' g</b>	ıl.	9.5	21.8	34.1

In the United States of America toluene's primary use is as a blending stock in high octane motor or aviation gasolene and benzene is a highly valuable chemical building block; price differentials between benzene and toluene are normally more than adequate to cover these costs. A similar situation may well develop elsewhere in the world.

Catalytic hydrodealkylation by the DETOL process thus provides the petroleum processor with an economically attractive means for upgrading lower value aromatics to benzene and provides an inexpensive entry into the production of aromatic chemicals to serve as a basis for a chemical industry. It should be considered seriously by developing nations in planning their petrochemical growth.

#### BENZENE BY HYDRODEALKYLATION USING THE DETOL PROCESS

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## **15. PRODUCTION OF AROMATICS FROM PETROLEUM IN JAPAN**

Isaburo Watanabe, Japan Gasolene Company, Ltd., Japan

#### INTRODUCTION

The tremendous petrochemical industry development in Japan dates back to December of 1957 when Mitsubishi Oil Company Limited began the aromatics production of benzene, toluene and xylencs from a light naphtha fraction of Seria Crude Oil, using a UOP Platforming-Udex combination unit. In the immediate sequence, Mitsui Petrochemical Industries Ltd. and Sumitomo Chemical Company Limited started the operation of their ethylene units in the spring of 1958. Thus, the overall petrochemical industry began.

In the petrochemical industry, since the aromatics, as well as the olefins such as ethylene, propylene, butylene, are absolutely necessary materials, it is essential to the development of the petrochemical industry to produce a large quantity of low-cost aromatics.

It is a normal practice to produce aromatics from the light naphtha fraction of aromatic or naphthenic base crude oil, using such a catalytic reforming-Udex combination unit as Mitsubishi Oil is operating. However, since sufficient amounts of aromatic or naphthenic base crude oils are not readily available in Japan, the recovery of aromatics from the ethylene by-product light oil has been commercially applied. Mitsui Petrochemical Industries Ltd. installed the first commercial unit of this type in the world; it is a combination of UOP Two-Stage Unitining and Udex Units.

In succession, Mitsubishi Petrochemical Company Ltd. and Nippon Petrochemicals Company Ltd. installed the same type of unit and the recovery of aromatics from the ethylene by-product light oil has increased rapidly in Japan.

Japan Gasolene Company is an engineering company and acts as a licensing agent for the Universal Oil Products Company in Japan. All of the aromatics production units from petroleum in Japan were engineered and constructed by the Japan Gasolene Company based on the engineering design of the Universal Oil Products Company.

### Amount of aromatics produced in Japan

Before petroleum aromatics were marketed in Japan in 1958, the production of aromatics was carried out exclusively by coke oven processors such as the iron and steel, town gas and chemical industries.

Figures I and II show the increase in the amount of aromatics produced in Japan since 1958. Figure I shows

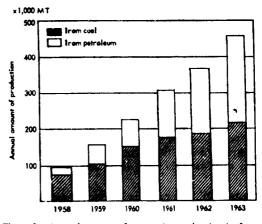


Figure 1. Annual amount of aromatics production in Japan

the increase in petroleum aromatic production, which was 22 per cent of the total amount of aromatics produced in 1958 in Japan and exceeded 50 per cent of the total in and after 1962. Figure 11 shows that benzene is the main product of the aromatics from coal but benzene, toluene and xylenes from petroleum are produced in almost equal amounts. This is due to the fact that the aromatics produced with a UOP Platforming-Udex combination unit contain,

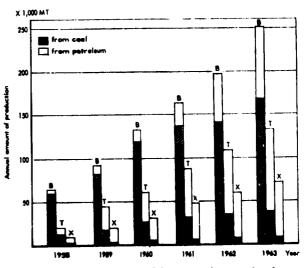


Figure II. Annual amount of benzene, toluene and xylene production in Japan

in general, a significant amount of toluene and xylenes and not large amounts of benzene, whereas the aromatics from ethylene by-product light oils contain a considerable percentage of benzene and lesser amounts of toluene and xylenes. Therefore, considering the production of petroleum aromatics as a whole, almost equal quantities each of benzene, toluene and xylenes are produced.

#### PRODUCTION OF AROMATICS BY UOP PLATFORMING-UDEX COMBINATION PROCESS UNIT

In Japan, Mitsubishi Oil Company Ltd. and Maruzen Oil Company Ltd. are currently producing aromatics from a light naphtha fraction by a UOP Platforming-Udex combination unit. Mitsubishi Oil started the initial operation of the unit using light naphtha of Seria Crude Oil as a feedstock, but has now changed the source of feedstock to a light naphtha from Bunju Crude Oil. Since the Platformer reactor feed obtained from Bunju Crude Oil contains about 73 liquid volume per cent of aromatics plus naphthenes, the aromatics content can amount to as much as 60 liquid volume per cent of the Platformate produced and, therefore, Bunju Crude Oil is very attractive for the production of aromatics. The capacity of Mitsubishi Oil's Udex Unit is 750 barrels per day.

Maruzen Oil Company is producing aromatics from North Sumatra Crude Oil and the aromatics plus naphthene content of the Platformer reactor feed is about 50 liquid volume per cent and the Platformate produced contains about 43 liquid volume per cent of aromatics. Each of Maruzen Oil's two Udex units has a capacity of 1,500 BSD.

Koa Oil Company Ltd. is also operating a UOP Platforming unit for aromatics production but Koa Oil's situation is somewhat different from that of Mitsubishi Oil Company and Maruzen Oil Company. When Mitsui Petrochemical Industries Ltd., which is located close to Koa Oil, planned to enter the petrochemical industry in 1957, they required a large amount of aromatics and decided to install a UOP Two-Stage Unifining-Udex combination unit to recover aromatics from an ethylene by-product light oil. However, since the amount of aromatics required could not be recovered from the ethylene by-product light oil alone, Mitsui Petrochemical purchased Platformate from Koa Oil and charged to the Udex unit a mixture of the purchased Platformate from Koa Oil and the Unifinate from the Mitsui's Two-Stage Unifining unit. Since, for some reason, Koa Oil is not

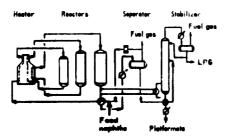


Figure III. Simplified flow diagram of Platforming process

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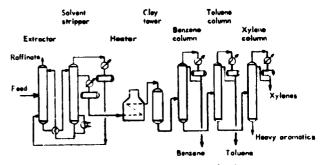


Figure IV. Simplified flow diagram of Udex process

able to obtain naphthenic crude oil and is producing a Platformate from paraffinic base Middle East crude oil, the Platformate contains considerably less aromatics than those produced by Mitsubishi Oil and Maruzen Oil. Recent developments in Platforming, however, have made possible high aromatic yields for the low naphthene Middle East fuels, making their consideration more attractive than was previously possible.

The present status of the production of aromatics in Japan has been outlined. Actual operating data, however, of the commercial units are not available because of their confidential nature and also because the operating conditions and the situation of crude supply of each company are different from those which prevailed when the operation started. Therefore, as a typical example of the production of aromatics from Seria Crude Oil, using a UOP Platforming-Udex combination unit, the economics of the process, assuming installation of a 1,000 BSD Udex unit, will be discussed, in the hope that this discussion will be of some assistance to the developing countries which plan to enter the petrochemical industry.

To assist in understanding the flow of the Platforming-Udex, a typical simplified flow diagram of the UOP Platforming-Udex combination unit is shown in figures III and IV. These process units are so well known that the explanation of the process is omitted.

Table 1 shows a material balance, table 2 the erected cost, table 3 the estimated utility requirement, and figure V the production cost of aromatics by the Platforming-Udex combination unit for this modest capacity.

#### RECOVERY OF AROMATICS FROM ETHYLENE BY-PRODUCT LIGHT OIL

In Japan, ethylene has been produced by the pyrolysis of a straight run naphtha. The pyrolysis unit does not produce ethylene alone; a light oil of the  $C_s$  + and heavier portion (400°F end point) it also produced as the pyrolysis by-product fraction.

Actually, the  $C_s$  + light oil contains a considerable percentage of benzene, toluene and xylenes, but this light oil also contains considerable olefins, which makes it a very unstable material. This unstable material could cause fouling problems in the processing equipment.

Universal Oil Products Company has developed the "Two-Stage Unifining Process-Udex Process" as a

TABLE 1.	Estimated Platforming and Udex yields	
	Seria light naphtha fraction	

Charge:	"API Boiling range Mol. Wt.	55.0 149-274°F T 99	9P	
Platform	ing charge		BSD	LV".
C, par	affins		100	8.4
C, par	raffins		188	15.9
C, par	raffins		102	8.7
C <sub>s</sub> nar	phihene		135	11.4
	phihene		290	24.7
C, ner	phthene		188	15.9
	ne		8	0.7
	ne 65	· · · · · ·	64 105	5.4 8.9
			1,180	100.0
Platfor m	ing products		(SCF/BBL)	( Mol. 🍫)
Н			(1,300)	( 95.5)
C			( 8)	( 0.6)
C			(20)	(1.5)
C			( 34)	( 2.4)
C <sub>s</sub> an	d lighter		(1, <b>362)</b>	(100.0)
<b>C.</b>			38	3.2
C <sub>6</sub> .			33	2.8
C <sub>4</sub> an	d C <sub>1</sub>		71	6.0
C. De	raffins		89	7.6
	rafins		151	12.8
	raffins		67	5.7
	phthene		40	3.4
C- na	phthens		30	2.5
C <sub>6</sub> na	phthene		9	0.8
Benze	ENG		83	7.0
Tolue	<b>me</b>		277	23.6
Xyler			254	21.6
	• •	Udex feed	1, <b>000</b> , 1	85.0
Udex p				
			<b>8</b> 2	
Tolu		• • • •	264	
Xyler		• • • • •	230	
Raffi	<b>Bait</b> .		426	
			1,000	

TABLE	2.	ESTIMATED US	A ERECTED	COST	()ł	PLATFORMING-
		UDEX (	COMBINATION	UNIT		

Platforming:	1,180 BSD	\$
Material		600,000
Labour		214,000
Design, engineering and con	itractor's expenses.	149,000
	TOTAL	963,000
Udex:	1,000 BSD	
Material .		775,000
Labour		354,000
Design, engineering and con		203,000
	TOTAL	1,332,000
Estimated paid up royalty:		
Platforming.		121,300
Udex		250,000
Estimated catalyst and chemi	cals investment:	
Platforming catalyst, R-5		20,200
		(est. CIF)
Glycol		14,000

The ethylene by-product light oil is first charged to a depentanizer, where a  $C_5$  cut is taken overhead. The bottoms product from the depentanizer is charged to the rerun column where the  $C_5$ + fraction is taken as a bottoms product and the  $C_5$ - $C_5$  "heart cut" fraction is taken overhead.

The "heart cut" is first mixed with hydrogen, heated and charged to the reactor section, consisting of No. 1 reactor and No. 2 reactor, where a specially prepared cobalt-molybdenum catalyst is loaded. In the No. 1

#### TABLE 3. ESTIMATED UTILITY REQUIREMENTS OF PLATFORMING-UDEX COMBINATION UNIT

	1,1 <b>20 BSD</b> Platforming	1,000 BSD Udex
I. Electricity, kWh		
Purses and compressor	. 300	124
Lights and instruments	. 15	15
2. Steam, ib/hr		
650 paig		530
130 paig		28,500
3. Cooling water, gal/min		
3 <b>5°F rise.</b>	. 600	1,600
4. Fuel, 10 <sup>e</sup> BTU/hr	. 20	
5. Chemicals, Ib/SD		
Platforming catalyst	. 15	
Caustic	. 250	
DEG	. 7	250
		390

solution to this problem. Since this combination process provides an ideal method for the recovery of aromatics from this unstable, difficult material, all the Japanese manufacturers of aromatics from the ethylene by-product light oil have used the Two-Stage Unifining-Udex combination process.

A brief description of the process flow of the Two-Stage Unifining Process will be given. The process schematic diagram of the Two-Stage Unifining unit is illustrated in figure VI.

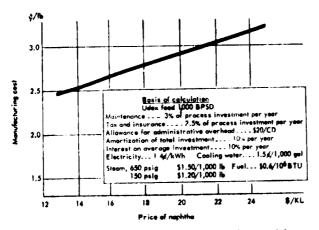


Figure V. Manufacturing cost of aromatics from naphtha by Platforming-Udex combination unit

reactor, the diolefins are selectively hydrogenated, thereby preventing polymerization reaction which may cause equipment fouling. In the No. 2 reactor, nitrogen and sulfur components are converted to  $NH_s$  and  $H_sS$ respectively and mono-olefins are completely saturated. The No. 2 reactor effluent is cooled and charged to the product separator, from which hydrogen is recycled to the reactors. The liquid from the separator is charged to the stripping column, where the hydrogen sulfide, ammonia, and light hydrocarbons are fractionated from the desulfurized light oil. The bottoms product from the stripper column is then available as a feed to the Udex unit for the extraction of high purity aromatics.

Table 4 shows the present status of aromatics production from by-product light oil in Japan. The total capacity of the Udex units in operation and under construction is 4,128 BSD and 8,250 BSD, respectively. In addition, four companies plan to install Udex or Sulfolane units and it is anticipated that the total capacity of the Udex and Sulfolane units for the production of aromatics

TABLE 4. CAPACITY OF UDEX UNIT PROCESSING STHYLENE BY-PRODUCT LIGHT OIL IN JAPAN

	In operation BPSD	Under construction DPSD
I. Mitsui Petrochemical Ind., Ltd.	1,700	1, <b>700</b>
2. Mitaubishi Petrochemical Co., Lid.	1,606	1, <b>890 *</b>
3. Nippon Petrochemicals Co., Ltd.	822	2,160
TOTAL	4,128	5,750
4. Identites Kosan Co. Ltd		2,500 *
		8,250

 Sufficience Process Unit based on basis design of Universal Oil Products Comments.

4

### TABLE 5. ESTIMATED TWO-STAGE UNIFINING AND UDEX YIELDS Ethylene by-product light oil

Charge: By-product light oil from Naphtha Pyrolysis unit which produces 50,000 metric tons per year of ethylene

Prefractionation charge	MT/yr (BSD)	W1. *•
C	12,500	20.0
Benzene	12,230	19.6
Toluenc	11,600	18.6
C, aromatics .	7,140	11.4
$C_1 + \ldots + \ldots + \cdots	8,480	13.6
C <sub>q</sub> -C <sub>s</sub> non-aromatics	10 <b>,490</b>	16.8
	62,440 (1,500)	100.0
Prefractionation products		
C. —	12,500 ( 370)	20.0
<b>C</b> +	8,480 (190)	16.8
Unifining feed	41,460 ( 940)	63.2
	62,440 (1,500)	100,0
Unifining charge		
Rerun overhead	41,460 ( 940)	99.4
Hydrogen (as 100 per cent H <sub>s</sub> ).	280	0.6
	41,740	1 <b>00</b> .0
Unifining products		
Gas to fuel	30	
Unifinate	41,710 ( 960)	100.0
	41,740	100.0
Udex charge		
Unifinate	41,710 ( 960)	
Udex products *		
Benzene	12,160 ( 260)	29.1
Toluene	11,020 ( 240)	26.4
C <sub>s</sub> aromatics	5,710 ( 120)	13.7
Raffinate	12,820 ( 340)	30.8
	41,710 ( 960)	100.0

lecoveries, vol. per cont Benmes = 99.5 + Toiuene = 95

C<sub>1</sub> aromatics - 30

from the ethylene by-product light oil will exceed 15,000 BSD in the immediate future. The Sulfolane process, developed by the Shell Development Company, is an extraction process for the separation and purification of aromatics from hydrocarbon mixtures employing Sulfolane as a solvent similar in principle to that of Udex. Universal Oil Products Company is the exclusive licensing agent of the Sulfolane process. It is anticipated that the development and use of this new process will lead to a reduction in aromatics recovery costs in the future.

The economics of the Two-Stage Unithing-Udex process unit is shown in tables 5 through 7. In general, the amount of the light oil produced and the aromatics content thereof varies, to a large extent, by the properties

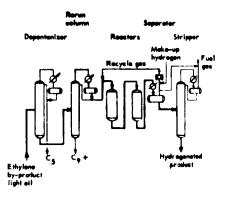
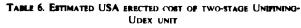


Figure VI. Simplified flow diagram of two-stage Unifining process

of the feedstock to the pyrolysis unit and also by the severity of cracking. Thus, the operating data vary with each manufacture. Therefore, tables 5 through 7 present a typical case; in other words, these tables show economics of a pyrolysis operation for maximum olefins yield from 100-350°F naphtha fraction of Middle East crude.



Prefractionation section:	8
Material and labour	280,000
Two-stage unifining unit:	
Material and labour	450,000
Udex unit:	
Material and labour	930,000
TOTAL material and labour	1,660,000
TOTAL material and labour Allowance for design, engineering and contractor's expenses	1,660,000 350,000
Allowance for design, engineering and contractor's	
Allowance for design, engineering and contractor's expenses	350,000
Allowance for design, engineering and contractor's expenses Total	350,000
Allowance for design, engineering and contractor's expenses Total Estimated paid up royalty: Unifining	350,000 2,010,000 19,000

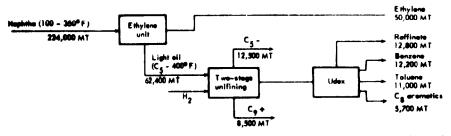
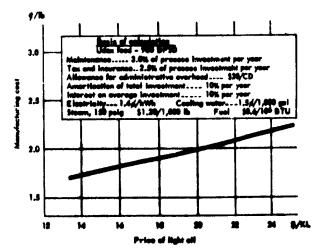
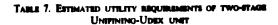


Figure VII. Blocked flow diagram of the recovery of aromatics from ethylene by-product light oil

Figure VII shows relationship of the feed and products in this case and figure VIII shows production cost of aromatics from ethylene by-product light oil.



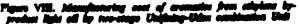


	Professionation and Unifinity	Viles
I. <b>Meetricity,* kW</b>	200	114
2. Cooling water, gal/min	1,409	1,000
3. Fuel gas,* 10 <sup>4</sup> BTU/lir	15	21
4. Steam (150 paig), 1,000 Ho/hr	3.7	
5. Chemicals Catalyst, 16/8D	26	
Gipeol, Ih/8D	-	201
Ciny, 16/8D	-	22

· Not all bolt included.

#### CONCLUSION

The processing technique of the Two-Stage Unifining-Udex combination unit may be noteworthy particularly for these countries where aromatic or anyhthesis crude oil is not readily obtainable.



# 16. OPTIMUM COMBINATION OF PETROLEUM REFINING AND PETROLEUM CHEMISTRY PROCESSES

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This report deals with the principal scientific and technological aspects of the problem of the optimum combination of petroleum refining and petroleum chemistry processes. The choice of variants depends on their economic advisability for a given geographical region.

The term "petrochemistry" is used to mean the production of synthetic materials based on petroleum raw materials. Among those products are: plastics, fertilizers, toxic chemicals and herbicides for agriculture, synthetic fibres and rubbers, detergents, high-quality resins, etc.

Although the production of these synthetic materials is developed rather well for specific processes, in most cases the problem of effective use of oil both for petrochemical synthesis and for petroleum refining or manufacture of motor fuels and lubricants is not solved as a single complex. One aspect is often developed at the expense of the other. Meanwhile, the modern level of science and technology permits the successful solution of the problem of utilizing oil and gas in both petrochemical synthesis and fuel-lubricant production.

The development of a given process depends on the chemical nature of available crude oil, on the need for the synthetics produced and on the high economic efficiency of petrochemical industries.

The principal hydrocarbons used for organic synthesis are lower olefins, parafiles and aromatics. There exist quits a number of processes for their manufacture.

In the Union of Soviet Socialist Republics, the organic synthesis industry has undergone radical changes: its development is more and more based on the use of petroleum hydrocarbons and natural gas.

The ever-growing development of the organic synthesis based on petroleum is going on in the industrially advanced countries as well as in the developing countries of Africa, Asia and Latin America. Thus, necerding to published data the quota of petrochemical production in the United States of America is continually increasing and it is expected that by 1965 its share will be 35 per cent and its cost will reach 66 per cent in the total volume of chemical production of the United States.

The growth of the organic synthesis industry gave rise also to the eight principal directions in the production of petroleum intermediates:

4

1. Olefin production by pyrolysis of lower parallins and straight-run low-octane gasolene fractions and nephtha distillates;

2. Catalytic reforming of gasolene fractions for aromatic production to isolate benarne, toluone, xylene and ethylbenzone;

3. Catalytic cracking of petroleum distillates with predominant formation of gaseous products;

4. High-temporature reforming of naphtha fractions to produce olefins;

5. Thermo-onidative pyrolysis and electrosuncking of methane to acetylene and synthesis gas:

6. Isolation of naphthonic hydrocarbons (cyclohexane, cyclopentane; and their derivatives) from gasolene of naphthonic crudes;

7. Isolation of parafine by molecular sieves, complexing and selective solvents;

8. Dohydration of individual paralla. (butane butylense, isopontane) to olofine and disease.

The following new processes of petrochemical synthesis are developed on the base of these hydrocarbon raw materials:

1. Polymerization and copplymerization of elefins. alkenylaromatics and dience, and polycondensation of bifunctional compounds of dicarboxylic acids with diamines and polyatomic alcohols to obtain plastics, synthetic rubbers and synthetic fibere;

2. Oxidation of parallas, clofins and aromatics to obtain acids, unides, aldehydes, hotones, alechols and perenides.

3. Onidative antenanolysis of olofins and aromatics to obtain nitriles;

4. Chlorination and hydrochlorination of parafilm, olefins and aromatics to obtain insecticides, herbicides, solvents and chlorinated monomers for manufacture of polymers, and openide resins;

5. Production of alkenylarometic compounds and monomers for the manufacture of thermostable plastice;

6. Production of methanol, summeric and uses from synthesis gas.

The processes listed do not, of course, cover all the assesses of rapid growth of petrochemistry, though as

a whole they meet the objectives determining the prospects within the next few years and are directly connected with the extended " unufacture of synthetic rubber, synthetic fibres and plastics.

Fundamental works of prominent Russian and Soviet scientists, D. I. Mendeleev, N. D. Zelinsky, I. I. Gubkin, V. V. Markovnikov, M. I. Konovalov, L. G. Gurvich and S. S. Namyotkin as well as of the scientists of the Azerbaijan S.S.R., Vu. G. Mamedaliev, V. S. Gutvrya, A. M. Kuliev, M. A. Dafin, and G. G. Ashumov in the field of examination and study of crude oils, helped to show the oconomic importance of oil and its unlimited opportunities.

Compared with solid useful minerals such as coal, shale and peat oil arc richer in hydrocarbons, easier to iransport, and easier to process. Oil and especially gas production is comparatively economical; their comprehensive use in the national sconomy is more effective and is accompanied by comparatively low capital investnient.

It should be home in mind that the economical development of a country depends not only on organic synthesis industries but equally on petroleum refining products such as fuels and lubricants. Oil refining and petroleum chemistry are two major industrial branches based on petroleum refining which determine the economic development of a country and which must be combined in a certain optimum. That is why oil must be evaluated in terms of its application in the whole technological complex and its potential as a source for the inanufacture of motor oils and lubricants as well as for petrochemical production.

The successful solution of this urgent problem depends on the availability of crude oil and a developed scheme of complex oil processing.

The optimum combining of technological processes in petroleum refining and petrochemical industries may be accomplished in different ways. In this report stress is laid on three principal variants of combining petroleum refining and petrochemical processes.

The first combination variant includes refining processes proper, aimed at obtaining fuels and lubricants (fuel-oil branch), and petroleurn processing of synthetic gnees accompanying crude destruction to make the organic synthesis products (chemical branch). Modern petroleum refining schemes combine a series of processes. Their choice is dependent on the quality of the product and the technical and economic results of the production.

The principal reference operation is oil dessiting, that is reducing the salt content of the oil to a minimum. This prolongs the on-stream period of subsequent units and ensures good quality of residual products obtained (fuel oil, bitumens, colte). Gasolene, kerosone and dissel fuels obtained by atmoopheric distillation are rid of objectionable impurities using alitali treatment, hydration and dewaxing followed by compounding with additives. If necessary, light geodene fractions undergo isomerination. The low-actane pertion of geolenes is catalytically refermed in order to upgrade their quality or to manufacture and-product aromation – beauene, toluenes and syleme.

Notable is the process of n-paraffin isolation with molecular sieves as well as microbiological dewaxing of middle paraffinic fractions to obtain protein-vitamin concentrates, which may be used as valuable feed for cattle-breeding. Work in the same direction is done abroad also by Avery, Lee and Alpert (United States of America), Champagna, Balaceano (France), Gilbert (United Kingdom).

The residue of atmospheric distillation, black oil, is distilled under vacuum to obtain the raw material for furthe, catalytic processing or raw oil distillates. In a number of regions, black oil is partly used for the manufacture of dark-coloured fuels and lubricants.

Depending on the chemical composition of the crude processed and on the requirements for the range and quality of lubricants produced, oil distillates undergo complex treatment including solvent extraction treatment by adsorbents, hydration, hydrogen treatment, dewaxing etc. Residual oils are produced from black oil vacuum distillation residues toil tars) by deasphaltization followed by cleaning and dewaxing. Commercial oils are compounded, using distillate and residual oils with a compulsory admixture of additives to improve performance, the latter additives being usually petrochemicals.

Heavy residual stocks from oil refining serve also for making electrode or fuel coke and road asphalt.

In recent years, hydrocracking is more and more extensively used in the Soviet Union for black oils processing. The same process is used to obtain middle distillates (diesel fuel) and vacuum distillates, coking products, etc. Similar work is done in the United States of America and other countries. Noteworthy in this respect are the works by B. Hansel, Politzer, Watkins. G. Scott, G. Robbers. H. Messon and others, S. K. Shuman and S. E. Slaingstad, Robert Bosk, Robert Dutrio and others from the Institut du petrole français, as well as studies by Watkins, Smith and Macloren on highly selective catalysts for hydrocracking. Secondary refining operations such as catalytic cracking, pyrolysis and reforming are also widely used. Catalytic cracking combines the interests of refining and petrochemical industries, providing highoctane gasolone and a number of lower hydrocarbons useful for petrochemical synthesis. Catalytic reforming, being a source of aromatized gasolene or of individual aromatic hydrocarbons, at the same time produces cheap hydrogen necessary for hydrocracking and hydrogen treatment. The pyrolysis profile has been greatly changed.

From being the source of aromatics it has turned into the source of unsaturated hydrucarbons: ethylene, propylene, butylene, and butadiene.

Destructive processes of oil refining form a reliable foundation for developing organic synthesis industry, with which they are closely limited. The chemical branch of the combinut processing scheme includes plants for processing gaseous paraffirs and olefine, aromatics as well as liquid paraffirs and paraffir wax. The details of this scheme are discussed below. As regards the optimum combination of refining and petrochemical processes, massion should be made of the combining of refining processes proper and petrochemical process which hes been widely used in recent years. Thus primary distillation is combined with electrodesalting, vacuum distillation of black oil, rerunning of long gasolene fraction, catalytic cracking of vacuum distillate. destructive distillation of oil tar, gas compression and adsorption, and gasolene stabilization.

Estimates showed that the cost of such a refinery is 46 per cent less than the cost of separate units, the floor area is reduced by 74 per cent, the staff by 65 per cent, steam consumption is halved, water consumption is reduced by 52 per cent, etc.

Another major trend in the design and construction of modern refineries is to enlarge the size of the units. According to estimates, such an enlargement considerably reduces the capital investment for building refineries. For example, by enlarging the output of an atmospheric vacuum tube heater from 2 to 6 million tons per year, the metal consumed per ton of crude processed was reduced by more than half and capital investment reduced by about 50 per cent.

As distinct from the above, another trend envisages the processing of natural and casing-head gases and gas condensates to obtain petroleum raw materials for their further use in petrochemical synthesis. The principal part of such plants usually contains units for fractionation of natural and casing-head gases and units for stabilization of isolated gasolenes, crudes or oil condensates. In practice, a number of methods for gas topping have found common application absorption, lowtemperature condensation and adsorption; combined processes are often used. Currently low-temperature condensation is preferred, because it increases the quantity of end products, which offsets somewhat greater expenses compared with other methods. Judging by literature on the subject the low-temperature gas topping is also widely used in the United States of America and other countries (B. G. Tacker) though detailed quantitative information is not available. The plants processing natural and casing-head gases produce dry gas used as an intermediate for chemical processing (thermo-oxidative pyrolysis, chlorination, catalytic conversion) or as fuel; ethane, propane and butane fractions mainly undergo pyrolysis or dehydration; stable gasolene is used either for aromatics or olefins production, or like diesel fuel it may find general use too.

The chemical branch of such plant includes petrochemical synthesis and is described in detail below.

The third combination variant envisages the complex use of cheap hydrocarbon resources: low-octane straightrun gasolines, condensates from gasolene plants, natural and casing-head gascs, and consists of three separate branches, based on the use of aromatics, olefins and parafilms.

The first branch includes low-octane gasolene fractionation and catalytic reforming of gasolene fractions 65 to 105°C and 105 to 140°C on platinum catalyst as well as extraction of aromatics and xylene inomers separation. Reforming of the said gasolene fractions gives aromatic hydrocarbons — bennene, toluene, ethylbonness and xylenes. The aromatics obtained undergo further chanical processing. Bennene is converted to ethylbonness

and styrene to phenol and acetone by cumene method, and is also used for agriculture chemicals. hexachlorobenzene and DDT Phenol is used for phenoi-formaldehyde resins manufacture, and for diphenylolpropane used in the synthesis of epoxide resins; a considerable part of it is also utilized in the manufacture of herbicides for agriculture.

Toluene is used for caprolactam manufacture; the latter serves as a raw material for polyamide resins and synthetic fibres.

Ethyltoluene is produced by alkylation of toluene; it is then dehydrated and polymerized to obtain polyvinvitoluene, a high-quality plastic.

The availability of a considerable excess of toluene makes it possible to demethylize part of it to benzene.

P-xylene is oxidized to terephthalic acid. It is then converted to dimethyl terephthalate, from which, by its polycondensation with monoethylene glycol produced in the same complex, polyethylene terephthalate is obtained, the last-mentioned being converted to polyester fibre.

The other two xylene isomers are also changed to chemicals: phthalic anhydride used for polyester resins manufacture (by condensation with diethylene glycol), phthalonitriles used for dyes and other chemicals as well as for polyvinylxylene type of polymers, promising thermostable plastics. In spite of the limited use of methaxylene some portion of it may be isomerized to p-xylene. Ethylbenzene produced in reforming is utilized in styrene manufacture.

According to P. Sherwood, aromatics are used for petrochemical syntheses in the United States of America in the same manner. Work on xylene isomerization is being done by Prof. Tsutsumi and there has been commercial manufacture of terephthalic acid in Japan.

The first branch of the work deals with nostic acid manufacture from head gasolene fractions (i.b.p. 65°C) by air oxidation with parallel formic and propionic acids production.

Organic acids manufacture by light gasolene oxidation is used in the United Kingdom (H. I. Stenley).

The second branch covers principal pyrolysis units (its raw materials are gasolene fractions), ethane and propane extracted from natural gas and gases from deetructive processes, as well as units for pyrolysis gas separation by condensation method and for purification of the principal end products of this process — ethylene, propylene, butylenes and butadiene. Ethylene is used for the manufacture of polyethylene, ethylene exide (converted into ethylene glycols and other products) acetaldehyde and ethyl alchebel.

Another valuable plastic, polypropylens, is made from propylene

Mention should be made of the morits of Zigler (Federal Republic of Germany) and Natta (Italy) in the development of low-pressure polymerization processes using organo-metallic catalysts for polyelelin manufacture.

Propylene is used also for a number of valuable products: acrolain, through which glycerol is obtained; propylene oxide, used for polyester resin and floatation agent manufacture; and acrylonitrile, used for nitrile rubber and synthetic fibres.

Acrylonitrile manufacture from propylene and ammonia is developing rapidly. Considerable work is being done in this direction in the USSR, in the United States of America and in the United Kingdom (H. I. Stenley). In view of the simplicity and economy of its new synthesis, acrylonitrile appears to be a promising starting material for the manufacture of quite a number of synthetics.

**Dutane-butylene fractions from pyrolysis and refinery** gases, after butadiene and isobutylene have been isolated from them, are dehydrated to butadiene and used in the manufacture of butadiene-styrene and polybutadiene rubbers.

In recent years in the USSR new kinds of rubbers of stereoregular structure have been manufactured, which are similar in properties to natural rubber and by some indices superior to it. Among them are polybutadiene and polyisoprene rubbers. Advances in the manufacture of these rubbers are reported also by R. Workmen and P. Sherwood (United States of America). In view of the recent advances in curing methods, othylene-propylene elastomers are of considerable interest. They may find wide application in the manufacture of tyres and rubber goods.

The third branch is created on the basis of natural gas utilization. It contains the principal natural gas topping unit isolating individual hydrocarbons — ethane, propane, butane, isobutane and pentane fraction. As a result of topping dry methane gas is also produced. Ethane and propane go to pyrolysis, butane to butadiene manufacture, isobutane undergoes dehydration and is then used in the manufacture of butyl rubber and polyisobutylene. Pentane fraction is utilized in the isoprene manufacture, the latter being used in polyisoprene and butyl rubbers. By hot chlorination of this fraction, hexaclorocyclopentadiene is obtained, a promising monomer for the manufacture of thermostable plastics and an active agricultural toxic chemical.

By thermo-oxidative pyrolysis of methane fraction of natural gas, acetylene and synthesis-gas are obteined.

According to the reports by C. Gobba-Cavana and F. Simonini (Italy), the Montecatiny company has developed a process of oxidative gasolene pyrolysis giving acetylene and ethylene. However, in our opinion, this method, which employs much more costly raw material, can hardly compete with acetylene production from methane, as is confirmed by the prevalence of the latter method in many countries.

The following products based on acetylene are envisaged: vinyl chloride and vinylidene chloride for PVC and synthetic fibres, trichlereethylene, vinyl acetate and polyvinyl acetate.

Synthesis gas is employed for the production of ammonia, which is a valuable intermediate for the manufacture of nitrogeneus fortilizors: ammonium nitrate, other ammonium salts and uren, which is also a good addition to the feed in cattle-breeding. Liquid ammonin has also found direct application in agriculture as a highly concentrated fortilizer.

Moreover, synthesis-gas is a source of methanol, which is then all oxidized to formaldehyde; its polymerization gives polyformaldehyde, a valuable and promising polymer.

The second route for methane fraction is its chlorination to such chlorine derivatives as methyl chloride, methylene chloride, chloroform and carbon tetrachloride.

Such a petrochemical complex is of high economic efficiency because of its favourable raw-material base, the cheapness and high quality of the starting hydrocarbon material, and the high degree of combination of production. The described variant of combining petrochemical enterprises may be changed depending on the availability of raw materials, end-product requirements, water and energy supply, reagents availability, etc.

In the USSR, concrete schemes of petrochemical works are based on the recent achievements of science in this field. Specifically in the Azerbaijan SSR, where crudes are migue in their quality, that is low-sulfur, and essentially low-paraffin and low-resin content, the oil refining with respect to the fuel-lubricant variant is carried out according to a specific scheme depending on the natural properties of oil. Their refining gives high yields of lubricating oils without dewaxing and without obtaining dark oil products such as lubricating black oils, fuel oils and motor fuels. Gasolene fractions obtained from the Azerbaijan crudes do not require catalytic reforming; kerosene and diesel fuel fractions need no hydrogen treatment, and necessary freezing and cloud points are obtained without dewaxing.

**Decause of the naphthenic nature of Baku crudes, it is** possible to isolate from them, simply by leaching, a considerable quantity of naphthenic acids, widely used in a number of industries and in agriculture.

About 90 kinds of oil products are produced in the Azerbaijan SSR, including more than 40 kinds of lubricating oils; 53 kinds of oil products are exported to 38 countries. Besides the wide range of fuels and lubricating oils and greases, the oil and gas industry of the Azerbaijan SSR, is an abundant source of hydrocarbon taw material for petrochemical synthesis. On the basis of the processing of this raw material, a large-scale petrochemical industry has been created and is being developed further. Its products are: ethyl alcohol, synthetic rubbers, styrene and polystyrene, polypropylene, ethylene and propylene oxides with their derivatives, glycerol, epoxide resins, phenol, acetone, synthetic detergents, synthetic fibres, ammonia, carbamide, toxic chemicals for agriculture herbicides and other products. about 60 kinds in all. A part of the chemical products is exported.

In the Soviet Union and, in particular, in the Azerbaijan SSR oil production refining and petrochemical industries have been cruated which are rapidly developing on a grand scale in the directions outlined above. Defore the revolution, Azerbaijan was an undeveloped country, backward in both cultural and economic aspects. After the April socialist revolution (1920) the Azerbaijan SSR took the socialist way of development and for a short period made unprecedented progress in its economics by purposeful increase of block gold production with the object of full value utilization of oil in the interest of national economy, by the optimum combination of refining and petrochemical processes. Thus in 1964 the oil production has been more than ten times greater than in 1920, and in 1970 it will increase by a factor of 15. There has been a corresponding increase in the volume of the petroleum refining output: the gasolenes output is hundreds of times as great, and lubricants tens times.

The developed complex petroleum processing scheme made possible the establishment of a large-scale petrochemical industry in the Azerbaijan SSR based on economic and cheap petroleum rsw material: the sverage annual increase within the last five years is about 25 per cent.

Every year the republic increases its capital investment for further development of oil production, oil refining and petrochemistry.

To meet the demands of newly built refineries and petrochemical plants for equipment, the Azerbaijan SSR has its own oil machinery industry as well as an electrotechnical and instrument industry. Their output in 1964 is 218 times greater than in 1920.

The Azerbaijan SSR might have achieved a greater economic development if in 1941-1945 all its resources had not been turned to gaining victory in the Second World War.

Characteristic for petroleum industries in the Azerbaijan SSR is that almost all the oil produced is processed within the Republic; this promotes the development of its economy and a sharp rise in the national income. For the welfare of peoples and the cultural and economic development of all countries and, especially, for developing countries it is necessary to process the oil within the country where it was produced, by designing developed schemes for oil and gas processing, taking into account the volumes of fuels, lubricants and other products as well as hydrocarbon raw materials necessary to establish the complex of petrochemical processes for production of the wide range of petrochemicals.

This principle opens the way for large-scale production of fertilizers and toxic chemicals necessary in agriculture with simultaneous development of industry.

Profits made by the domestic oil processing industry might help these countries to solve housing problems sooner, and to increase the allocations for public health, social maintenance and education.

Realization of all these measures is a necessity dictated by the vital interests of millions of people in these countries.

Even if the processing G' all extracted oil offers some difficulty in sale (absence of markets within the country and in neighbouring countries) it is advisable, from the point of view of the increasing national income, not to sell crude oil, not to depreciate this valuable product, but to set up national firms for oil processing and organic synthesis in the foreign countries where there are markets for those products.

The use of petroleum on this principle, its processing by national companies, is more advantageous for the national income than selling oil in the place of its production. There is a considerable profit from selling commercial products of oil refining and petrochemical industries.

# 17. HYDROCARBONS STEAM REFORMING, IN TUBES, FOR PRODUCTION OF SYNTHESIS GAS OR HYDROGEN

### A. Roche, Office National Industriel de l'Azote, and J. Lemaire, G.E.G.I. Company, France

For some ten years, the use of gaseous hydrocarbons (particularly natural gas and refinery gas) or liquid hydrocarbons (light petrol or heavier products) as feedstocks for the production of hydrogen has been universally generalized and has practically replaced the use of coal or coke.

### 1. Main cracking and reforming processes

Several processes have been used. The main ones may be classified into two major categories: cracking with oxygen and reforming with steam.

### 1. CRACKING WITH OXYGEN

The reaction essentially consists of hydrocarbon conversion, by partial combustion with air, oxygen or superoxygenated air.

This combustion brings the necessary heat to the simultaneous conversion of the remaining hydrocarbon, by the products to which it gives rise (carbon dioxide, steam).

A small quantity of steam is generally added to inhibit the hydrocarbon dissociation reaction in its components: carbon and hydrogen.

The global reaction is autothermic.

In this category of processes, one must make a distinction between the thermic processes and the catalytic processes.

The thermic processes include, generally, the introduction, in a reaction chamber, of a mixture of hydrocarbon, oxygen (or super oxygenated air, if the presence of nitrogen in the final gas is wanted) and steam.

The reaction takes place at a high temperature; it is accompanied by the formation of a certain amount of carbon-black, which is eliminated in an appended apparatus.

The efficiency is relatively low, but processes of this kind have the advantage of being able to deal with all the hydrocarbons, including heavy oils and crude oils.

The catalytic processes include the introduction of the mixture hydrocarbon exygen and steam in a reaction chamber filled with an appropriate catalyst.

The use of this catalyst makes it possible to lower the reaction temperature and stop the formation of carbon-black completely. The result is greater efficiency

than in the thermic processes, but it is necessary to use relatively clean feedstocks, having a low sulphur content; in fact, it is possible in this case to use all the gaseous hydrocarbons and also the light petrols.

With thermic processes as well as with catalytic processes it is possible to operate under pressure, but it is then necessary to produce oxygen in an adjoining plant.

### 2. REFORMING WITH STEAM

In these processes, it is no longer necessary to have oxygen.

It is difficult to describe the reactions; nevertheless one can say that the conversion by steam always leads towards an ideal global reaction which would be the following:

$$C_n H_m = n H_2 O = n CO = \binom{m}{2} = n H_2$$

obtained through the medium of complex reactions. Besides, it is never possible to eliminate completely the methane and, in fact, the gaseous mixture always includes some carbon dioxide, carbon monoxide, hydrogen and methane.

All these reactions follow the classical reaction,

$$CO + H_{p}O \rightleftharpoons CO_{p} + H_{p}$$

Whatever it may be, the reaction is always carried out on catalyst: being an endothermic reaction it is necessary to bring the required heat from the outside source.

Owing to the different methods used to obtain these heating requirements, it is therefore possible to differentiate between the cyclic processes and the "tubes" processes.

In the cyclic processes, the operation consists of two main phases: a production phase during which the hydrocarbon and the steam are introduced in the cracking chamber filled with catalyst and a heating phase during which hot waste gases go through the catalyst bringing in the required heat.

The cyclic processes make it possible to use practically all the hydrocarbons [the matter being natural gas or ranging from natural gas to heavy fuel oil or crude eil. In the heating phase, during which excess air is introduced, the impurities deposited on the catalyst during the production phase are removed.]

The cyclic operation requires working at pressures very mean atmospheric pressure.

In the "tubes" processes, the catalyst is introduced in tubes situated inside a chamber and the heating is performed by burners, which are placed around these tubes.

Such processes require an extremely clean hydrocarbon; they were, until recent years, exclusively reserved for gaseous hydrocarbons, but some of them are now using light petrols.

In the "tubes" processes, it is possible to work either at pressures near atmospheric pressure or at higher pressures of about 30 atmospheres.

The processes of this type have therefore the double advantage of not using oxygen (which plants are usually expensive) and of being able to work under pressure; they are described in more detail in what follows.

# 1). Succinct description of the reforming apparatus

### 1. REFORMING CHAMBER

Such a chamber is made of a steel plate body, lined inside with refractory and insulating materials. The tubes containing the catalyst are disposed vertically inside this enclosure. They are made of highly refractory steel, cast by centrifugation. Their length is of about 10 metres and, according to the pressure used, the diameter varies between 100 and 200 millimetres. The number of tubes inclosed in the same chamber varies with the yield capacity but, in all cases, the gas made in each of these tubes is brought in a main pipe and sent to the following apparatus.

The burners can according to conditions use as fuel natural gas, refinery gas, propane etc. or light petrol alongside the wall of the chamber. The waste gases leaving the chamber go through a heat exchanger before being sent to the atmosphere through a stack.

The catalyst must be of the first quality, not only as regards chemical activity to prevent, in particular, all risks of carbon-black formation, but also as regards mechanical strength. The strength must permit use for a long period without any notable loss of activity.

### 2. POST-COMBUSTION CHAMBER

When reforming takes place in the tubes, under relatively high pressure, the gas made contains, in accordance with the balance displacement laws, a certain amount of methane; this methane content is, for pressures from 20 to 30 atmospheres and temperatures of about 700" to 800"C, of the order of 7 to 8 per cent. For the ammonia synthesis, it is necessary to lower the quantity of methane in the synthesis gas and also to introduce into this gas the nonseary nitrogen. This double operation is often made in a post-combustion chamber filled h catelyst, into which is introduced, at the same time as the reformed gas coming from the tubes, the necessary air. This chamber is made of a steel plate body lined de with refractory and insulating materials and inei naturdos a gas and air minor, and, generally, two sole plates to support the estabyt.

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### 3. DESUS PHURIZATION VESSEL

Reforming in tubes can only be conducted with a perfectly desulphurized hydrocarbon; otherwise the reforming catalyst would very quickly become worthless. The desulphurization of the hydrocarbon used is then of great importance. It is made on a zinc-oxide contact-mass at about 400°C (in some cases it is possible, with appropriate catalysts, to lower this temperature). This contact-mass is deposited in a special vessel made of steel plate and insulated externally. It must permit virtually complete desulphurization as it is necessary to lower the total content of sulphur (organic sulphur and SH<sub>B</sub>) of the hydrocarbons to a value of less than 1 ppm.

When the hydrocarbon used is light petrol, the petrol vapour desulphurization takes place in the presence of hydrogen obtained by the recycling of a small part of the final gas. In addition to great chemical activity, the contact-mass must have both a sufficient sulphur absorption capacity (so as not to be saturated too quickly) and sufficient mechanical strength (for handling operations). It is shown that with the contact-mass used in the ONIA-GI process a consumption of 4 kg of contactmass per 1 kg of sulphur is necessary in order to process the feedstock to be dealt with.

Usually, it is only necessary to desulphurize the hydrocarbon used in gas production (about 70 per cent of the total hydrocarbon) with the exception of the hydrocarbon used for heating. Generally, the size of the desulphurization vessel is expected to permit operation for about one year without having to interfere with the contact-mass.

### 4. COMPLEMENTARY APPARATUSES

Of course, these apparatuses depend on the feedstock, used and on the quality of the final gas to be obtained. They can include, on the gas-made circuit, plants for carbon oxide conversion, for methanation etc., and both on the gas-made circuit and on the heating wastegases circuit, apparatuses for recovering the sensible heat, such as: waste-heat boiler, steam superheater, water economizer, eventually petrol vaporizer and superheater, air superheater, etc.

### III. Industrial applications

Three possibilities for the use of the tubes reforming are given below. It is evident that these processes are capable of numerous other uses.

# 1. PRODUCTION OF SYNTHESIS GAS PROM NATURAL GAS ---- PRINCIPAL DIAGRAM

Such a plant can be made to follow the diagram shown in figure I. It includes essentially: one desulphurization vessel, one natural gas/reaction steam miner, one reforming vessel, one post-combustion chamber, one "process" waste-heat builer, one primary CO conversion chamber, one steam superhester, one netural gas hester, one water-economizer, one secondary CO conversion chamber, one "waste gases and wate heat" beiler, and one nir bester.

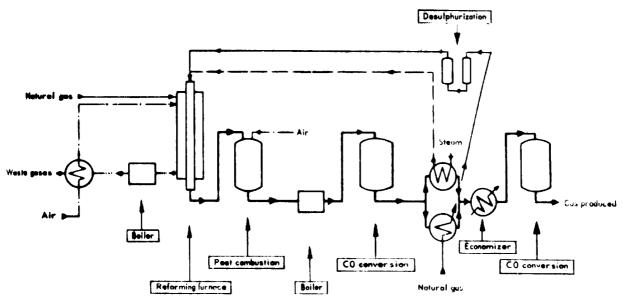


Figure 1. Production of synthesis gas from natural gas

After a suitable temperature is achieved, the operation Consumption per 100 Nm, of pure hydrogen is as follows

Processing stage. The reforming natural gas, previously heated, is desulphurized and then, after being mixed with superheated steam, it is introduced in the reforming vessel tubes where the reaction takes place; the gas produced goes through the post-combustion chamber where, with some air addition, the reaction ends, then through the waste-heat boiler, which permits the lowering of the gas temperature to a value suitable for the primary CO conversion, and finally the secondary CO conversion. The product gas is then available, in the case considered, at 220°C and 20 effective atmospheres.

Heating stage. The sir and the heating natural gas are sent to the reforming vessel burners; the waste gases produced move round the tubes; then, at the vessel outlet, they go through the "waste gases" waste-heat boiler and the air heater.

Operation results. If the natural gas having the following volumetric analysis is available at a pressure of 25 effective atmospheres for the processing stage and at a pressure of 6 effective atmospheres for the heating stage:

CH.											93.2
C.H.											4.0
											1.5
											1.3
•											
											100.0

The main operation results are as follows:

### Product-one unknowinks composition

17.80											0,	(
0.30						,			7		0	(
61.40			,								<b>L</b> .	1
0.37											ж,	
2.0											<b>i</b> , .	1
0.33											Ν.	1
1000.000												

Natural gas (reforming heating) (Nm <sub>a</sub> ) Electric power (kWh)				44.8 1.07
Purified and degasified water (litres) .	•	• •		158
Excess steam produced (25 eff. atmospheres saturated) (kg)			,	28
tate of the gas made at the plant outlet				
Effective pressure (atmosph.)				20

Effective pressure (atmosph.)	· · ·	20
Temperature (°C)		220
Water content (kg/Nms of dry gas)		0.45

### 2. PRODUCTION OF SYNTHESIS GAS FROM LIGHT PETROL

### Principal diagram

The plant can be made to follow the diagram shown in figure 11. It includes essentially: one reforming vessel, one post-combustion chamber, one waste heat boiler, one CO conversion chamber, one heat-exchanger, one steam superheater, one petrol vaporizer, one desulphurization vessel and one heat-exchanger for "waste-gases".

After achieving a suitable temperature, the operation is as follows:

Processing stage. The petiol is vaporized and desulrized (in the presence of a small quantity of recycled e). The stoom is added and the mixture petrol/stoom ed to the catalyst through the reforming vessel The process gas goes through the post-out ion ondo; the waste-heat boiler re the read p the gas to a suitable temperature for CO seaver-in the CO conversion chamber.

y stage. The wests press obtained by light petrol ion, in broving the reforming vessel, successively ch: the steam superheater, the patrol v a host-enchanger.

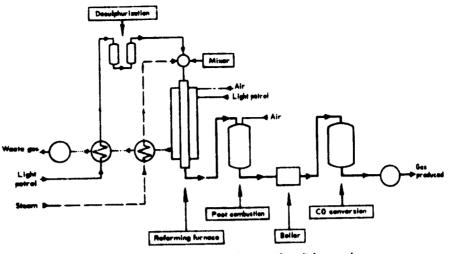


Figure 11. Production of synthesis gas from light petrol

100.0

In the case considered, the gas leaving the plant is available at 20 atmospheres and 180°C.

### **Operation** results

Assuming the use of a light petrol similar to those usually found in western Europe, the main operation results are as follows:

Gas made volumetric composition:

CO <sub>1</sub>																			19.8
<b>CO</b>	• •	·	•					į											3.0
Н,	• •	•	•	·	•	Ċ	•	·	•										58.0
CH <sub>4</sub> + A		·	·	•	•		·	•	•	·	·	·	•				Ż		0.5
N <sub>2</sub> · ·	•••	•	•	·	•	·	•	'	·	•	·	•	•	Ċ	÷	÷	÷		18.7
M <sup>8</sup> · ·	• •	•	·	·	•	•	•	•	•	·	·	·	•	•	•	·	•	•	

Commption per 100 Ning of pure hydrogen

Petrol (reforming + hosting) ()	(g)					35.4
Electric nower (kWh).					•	6.87
						Autonomy

State of the gas made at the plant outlet

Effective pressure (atmosph.) .		•	٠	·	·	•	·	٠	٠	·	
Temperature (°C)		•	•	•	٠	•	٠	٠	•	•	199
Water content (kg/Nmg of dry s	<b>, (an</b>	•		•	•	•	•	•	•	•	0.40

(a) The plant described in this case includes a conversion chamber lowering the gas CO content to 3 per cent. It is of course possible, as in the preceding case, to provide for a secondary conversion to lower this CO content further to a much lower concentration as for instance 0.3 per cent.

(b) in the two cases mentioned above, the gas is available at about 200°C, which corresponds to the temperature for the usual treatments of the product gas. It is of course possible to each the product gas more completely, if desired.

# 3. PRODUCTION OF PURE HYDROGEN FROM LIGHT PETROL

### **Principal** diagram

For this problem, it is necessary to exclude the use of a post-combustion chamber to lower the methane content of the gas leaving the reforming vessel because, unless pure oxygen is used, such mode of operation would introduce some mitrogen in the product gas.

To obtain a low methane content, it is then important to carry out the reforming under low pressure. A plant can be made to follow the diagram shown in figure III, which includes essentially:

### Cracking and first conversion at atmospheric pressure

- On the gas processing stage: the tubes reforming vessel, a gau-heater, a CO conversion chamber, a gas tubular cooler:
- On the water-gases stage: a steam superheater, a petrol vaporizer;
- A desulphurization unit.

# Product gas treatment under 25 atmospheres pressure

A gas-compressor, a first water washing-tower, a CO conversion chamber, a gas/gas heat exchanger, a second water-washing tower, a methanation chamber and a final cooler.

After achieving a suitable temperature, the operation is as follows:

Cracking and first CO conversion. After vaporisation and addition of a small amount of recycled gas, the petrol is desulphurized.

The mixture deculphurined petrol/superheated steam is introduced into the reforming vessel tables.

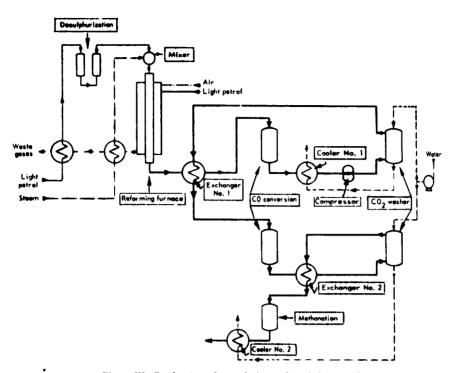


Figure III. Production of pure hydrogen from light petrol

The gas leaving these tubes goes through the heatexchanger and the CO conversion chamber, where its first conversion takes place.

The tubular cooler cools the product gas from the first part of the plant.

**Product-gas treatment.** After passing in a small holder, the gas leaving the first set of apparatuses is compressed at about 26 atmospheres and successively goes through: a first water-washing tower (removal of  $CO_2$ ), the gas/gas heat-exchanger set at the reforming vessel outlet, the second CO conversion chamber, a gas/gas heat exchanger allowing the recovery of heat for the methanation, a second washing tower to eliminate  $CO_2$ , the exchanger mentioned above, a methanation chamber to remove the last traces of CO, and a final cooler fed with the water from the second washing tower.

In the possibility considered, the hydrogen produced is available at about 25 effective atmospheres and 25°C.

### **Operation** results

If a light petrol having the following characteristics were used:

Specific gravity at 15°C												0.71
<b>Distillation: Starting point</b>												
Final point .												
Gross calorific value	•	•	•	•	•	•	•	•	•	•	•	11,450 mi/kg
Total sulphur content												
С/Н												
Aromatics content												
Olefins content			•									1 per cent

the main operation results of a plant following the diagram shown in figure 111 are as follows:

Gas made volumetric composition

H <sub>1</sub> ,						99. 0.	-
						100.	0
CO							ppm ppm
Consumptions per 100 N	im <sub>a</sub> oj	( pure	<b>h</b> ydrogen				
Light petrol (reformi	n <b>s</b> -t	heatin	ng) (kg)				32
Electricity (kWh).							33
Dry satured steam all	5/6 .	off. atn	noeph. (kg)	• • ·			135
Dry saturated steam	at 30	off. at	moeph. (kg	)			125
Washing and cooling	raw	water	(Nm <sub>s</sub> )	• • •	• •	•	12
State of the hydrogen at	the p	plant o	utiet				
Pressure (atmosph.).							25
Temperature (°C).				• • •	• •	••	25

### **IV.** Conclusions

With the tubes reforming processes it is possible to obtain, under pressure and without using oxygen, all the synthesis gases rich in hydrogen. (They are also used for tewn gas production, but this is not relevant to the present study.)

The fact of operating under pressure permits a notable saving of the electric power used for the gas compression before synthesis. The elimination of the oxygen plant reduces the capital costs and facilitates the operation of work. The reforming plants are simple and easy to operate: for processing synthesis gas corresponding to the production of 500 tons per day of ammonia, it is necessary to have 3 men per shift.

The operation results mentioned in the three cases outlined above give an idea of the cost price of the hydrogen produced. Of course, it is necessary to add the investment costs, which depend on the production capacity, the pressure, etc., and the price of catalysts, which is not very important. In the case of a hydrocarbon

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with a high sulphur content, the price of catalysts becomes important because the desulphurizing-mass costs approximately \$ French francs, and it has been mentioned earlier that 4 kg of mass are needed to remove 1 kg of sulphur from the hydrocarbon entering reaction.

In conclusion, it must be recalled that the development of such processes has been made possible thanks both to the metallurgy processes which now put at our disposal very high quality tubes and to the development of very high performance catalysts, for reforming as well as for desulphurization.

# 18. SELECTED PROCESSES FOR THE PRODUCTION OF BASIC CHEMICALS AND INTERMEDIATES FROM PETROLEUM HYDROCARBONS

# H. Sönsken, Badlache Anilin- & Soda-Fabrik AG (BASF), Federal Republic of Germany

The rapid growth of the chemical industry, particularly in the field of plastics, has given great impetus to petrochemistry, the production of raw materials from petroleum. It is small wonder that chemical manufacturers have devoted themselves to the development of techniques for the production and exploitation of these raw materials. Many new processes have come into being; older ones have been improved and adapted to suit the raw materials situation. Even countries which are just beginning to build up a chemical industry are making greater use of these modern techniques.

Important raw materials are comparatively few in number. Apart from hydrogen, carbon monoxide, and a few inorganic substances, such as alkalis, chlorine, and sulphuric acid, they consist essentially of acetylene and olefins, e.g. ethylene, propylene, and butadiene. A demand also exists for aromatics such as benzene, toluene, xylene, and naphthalene.

In order to keep pace with the trend towards reduced costs, larger production units have been designed. The simultaneous production of many substances in the one process and the great demand for a higher degree of purity entail extensive separating facilities and wellplanned, yet expensive, process control techniques. Capital expenditure is thus extremely high. As opposed to this, less personnel are required, but the operators must be highly skilled.

This paper describes a number of processes that have been developed in the Federal Republic of Germany. It is presumed that the processes themselves are known, and so only the underlying principles will be dealt with. Economic aspects will be stressed, and particularly important consumption figures will be quoted. This will allow the processes to be compared with others that were developed for the same purpose. It is fully appreciated that a deeper study would be required for an exact comparison and that local conditions, including economics, would be a major factor in deciding which process would be aslocted in a particular district.

The choice of the processes to be discussed in this paper was restricted to those for which a licence already exists or has been applied for.

- Production of hydrogen and synthesis of annualis (BASF Pressus)
- 11 Production of asstylene
  - 1. Montris are pressue (Chamiasho Warks 1988a)
  - 2. Partial esidation of indreambons (BANP)
  - 3. HTP Press (Farbwarks Heaster)

III. Production of ethylene

- 1. Authothermic cracking of crude oil in fluidized beds (BASF)
- Recovery of mono-olefins from mixtures of gases and purification of olefin fractions by selective hydrogenation
  - Recovery of mono-olefins with the aid of metallic salt solutions (Farbwerke Hoschst)
  - 2. Purification of olefin fractions by selective hydrogenation (Farbonfabriken Bayer)
- V. Processing of C4 fractions and recovery of pure butadiene
  - I. Extraction of butadiene from C<sub>4</sub> fractions by means of N-methylpytrolidone (BASF)
  - 2. Separation of isobutylene from butenc fractions (Farbenfabriken Bayer D.I.B. Process)
- V1. Manufacture of intermediates
  - 1. Production of acetaldehyde from ethylene by the Wacker-Hoechet Process
  - 2. Direct oxidation of ethylene to ethylene oxide (Chemische Werke Hüls)
  - Oxidation of butane in the manufacture of aliphatic acids and solvents (Chemische Worke Hülts)
  - 4. Production of alcohols and ketones from olefins (Rheinpreuses AG)

### 1. PRODUCTION OF HYDROGEN AND SYNTHESIS OF AMMONIA

Our reasons for beginning with the production of hydrogen for the synthesis of ammonia were not based entirely on the great significance attached to ammonia and nitrogenous fertilizers; allowance was also made for the fact that the production of hydrogen represents one of the very first petrochemical processes. While hydrogen was still being manufactured in Europe from coke oven gas, i.e., from coal, BASF developed a process for manufacturing CO + H<sub>1</sub> from methane or from natural gas (1). This tube cracking process consists of converting methane together with steam at temperatures of between 700° and 750°C over an externally heated highly active nickel estalyst to yield a CO + Ha mixture with a residual CH, content of about 5 per cent. The remaining CH<sub>4</sub> is subsequently converted in a type of shaft furnase by combustion with air over a catalyst with a low nickel content. The final content of CH, in iess than 0.2 per cont, and the process oneuros that hydrom and nitrogen are mixed together in the ratio rogu for the ammonia systhesis, i.e., 3 Ha: 1 Na

The first industrial-cashe plant operating on natural gas by this method was taken on stream in 1931 in Baten Roum. Louisiana, and consisted of three primary refermers, each with 66 tubes. The Chemical Construction Corporation developed the process a stage further, modifying the design of the reactor. Nowadays, more than 70 per cent of the synthesis gas used for the production of ammonia in America is manufactured by this means. An innovation introduced by ICI consists of employing the process for cracking light naphtha under pressure.

The principle of employing a type of shaft furnace as a secondary reformer gave rise to the BASF furnace for flame cracking, in which methane and oxygen are converted in the presence of steam by means of a partial combustion. In other words, a flame of pure oxygen, or air enriched with oxygen, is allowed to burn in a stream of methane and the gaseous products of partial combustion are passed over a catalyst with a low nickel content (2). Not only is this furnace capable of processing methane containing sulphur, but it also allows almost any gas in which hydrocarbons are present to be converted: refinery gases, producer gas, residual gases containing methane, etc., all of them being converted to CO + H<sub>1</sub> mixtures with or without nitrogen. The temperature to which the gas feedstock is preheated must be adjusted to make allowance for the cracking limits of the hydrocarbons in question. In view of the heavy soot deposits formed, gas feedstocks containing more than 40 per cent C have to be diluted by recycling.

A tube furnace with 66 tubes has a hourly capacity of about 10,000 m<sup>3</sup> STP of CO + H<sub>a</sub>. The amount of methane required to produce each 100 m<sup>3</sup> of CO + H<sub>a</sub> is 41.5 m<sup>3</sup> STP, in which case the methane also serves to heat the tubes. If another heat carrier is employed, only 30.3 m<sup>3</sup> STP of CH<sub>4</sub> are required.

The hourly capacity of a flame cracking furnace is of the order of 9,000 m<sup>3</sup> STP of CO + H<sub>1</sub>; for each 100 m<sup>3</sup> of CO + H<sub>2</sub>, 27.1 m<sup>3</sup> of CH<sub>4</sub> and 19.6 m<sup>3</sup> STP of oxygen, part of which may consist of air in the case of synthesis gas for ammonia, are required.

Autothermic cracking of hydrocarbons is made possible by a flameless catalytic process with oxygen, which entails partial oxidation without troublesome soot formation. It differs from the flame process in that the mixture of hydrocarbons, steam, and oxygen reacts exothermically over a platinum catalyst first of all. The subsequent procedure is similar to the flame process, the mixture reacting endothermally over a nickel catalyst to form CO + H<sub>2</sub> together with some CO<sub>2</sub> in an amount corresponding to the water gas equilibrium. Plants of this description are on stream in the BASF processing netural gas and waste gases containing hydrocarbons. They are also capable of cracking naphtha.

The amount of  $CH_4$  consumed in producing 100 m<sup>2</sup> at STP of  $CO + H_3$  is 34.5 m<sup>2</sup> STP. In addition, 17 m<sup>2</sup> STP of oxygen, either in the pure state or mixed with air, are meeded. The quantity of steam required from outside sources is 23.4 kg.

Autothermic cracking of hydrocarbons at atmospheric pressure is the more economical procedure if the raw materials are expensive, because it gives rise to the highest yield of CO + H<sub>3</sub> per unit weight of hydrocarbon. These remarks are valid regardless of whether or not finme evolving is resorted to. The reduction is yield estailed

in high pressure processes would not cover the savings in compression costs. In tube processes with external heating, the hydrocarbons employed for heating are lost for the purpose of synthesis gas manufacture.

All that need be said on the Haber-Bosch process, which accounts for more than 80 per cent of the world production of ammonia, is that it represents the result of more than fifty years of development (3). BASF, who introduced the process, have erected many modern ammonia factories throughout the world since the Second World War. A number of other BASF processes are closely associated with the ammonia synthesis in that they give rise to gaseous by-products that can be made to yield synthesis gas for the pro- Lon of ammonia.

### 11. MANUFACTURE OF ACETYLENE

### 1. Electric arc process

One of the oldest petrochemical processes is the cracking of methane in the electric arc to yield acetylene (4). The initial trials were run by BASF in 1925, and acetylene was first produced by this means on a large scale in 1940 by Hüls, who have been responsible for developing the process to its present-day state.

It is a two-stage process, the first comprising the production of pure acetylene together with crude ethylene and hydrogen. The pure ethylene is recovered in the second stage.

The electric arc is the focal point of the process. The hydrocarbon feedstocks to be cracked consist of natural gas, refinery gas, liquid gas, and light naphtha. The calorific value of these can be efficiently exploited before the water quench by injecting into the hot gases a certain amount of liquid hydrocarbons that favour the production of ethviene.

Most of the soot formed in the electric arc is removed and the remainder is recovered wet by scrubbing the gas. After a further scrubbing with water to remove hydrocyanic acad, the gas is compressed to 260 pei, at which pressure the acetylene is removed. Acetylene-free gases escape at the head of the tower, and a saturated solution of acetylene is drawn off from the bottom, where it is led off to be concentrated in four stages. Higher acetylenss are removed in a three-stage intensive cooler, after which the acetylene has a final concentration of 97 per cent and is perfectly dry. The gases leaving the head of the column at 240 psi are separated into the constituent hydrogen, hydrocarbons, and crude ethylene. The hydrocarbone thus recovered, together with a certain properties of the hydrogen, are recycled to the electric arc, being mined with the foodstock in order to ensure a given C-value. Excess hydrogen can be used for hydrogenation.

The analysis of a typical gas fed to a commercial-scale electric arc is given in table 1. If a further 120 kg of liquid gas per 1,000 kWh of energy commend (consisting of 25 kg C<sub>2</sub>H<sub>0</sub>, 60 kg C<sub>2</sub>H<sub>10</sub>, 35 kg ine-C<sub>4</sub> H<sub>10</sub>) are injected into this gas, the cracked products indicated in the second row in the table would be obtained.

TABLE 1. CONSUMPTION OF A GABBOUS PREDSTOCK TO WHICH 120 KG OF LIQUID GAS \* WAS ADDED FOR EACH 1,000 KW OF ENERGY CONSUMED AND THE RESULTANT CRACKED PRODUCTS

	с,Л,	с,и,	с <b>.</b> И,	с <b>.н.</b>	с <b>, Л</b> ,	с,н,	С.И.	с.Ж.	си,	с,И,	с,и,	€ <b>, H</b> ,,	с <b>, н,</b>	C.H.	(, <b>N</b> ,	<i>H</i> 1	<i>co</i>	N,
Gaseous feedstock (% vol) Cracked gas (% vol)												12.5 2.1					0.8 0.7	

\* 25 kg C<sub>2</sub>H<sub>4</sub> — 60 kg C<sub>4</sub>H<sub>14</sub> --- 35 kg ino-C<sub>4</sub>H<sub>14</sub> .

When allowance is made for losses, the amounts of feedstock and cracked products indicated in table 2 are obtained.

The considerable advantages of the acetylene/ethylene electric arc process are that it allows great scope in the choice of feedstock hydrocarbons and that all unconverted hydrocarbons or cracked products can be recycled. Even higher actelylenes, which are recovered in amounts of 10 per cent vol., expressed as a percentage of the  $C_{\rm B}H_{\rm B}$ , are returned to the electric arc. The electric arc is also capable of processing other hydrocarbon by-products. It is of interest to countries with cheap electricity, but large units are required to render it economically justifiable.

## 2. Partial oxidation of hydrocarbons

The partial oxidation of hydrocarbons, a process developed by BASF for the production of acetylene, is gaining in popularity (5). Suitable feedstocks are natural gas, refinery gases, light naphtha, and other gaseous and volatile hydrocarbons. The high cracking temperatures required are attained by oxidation of some of the hydrocarbons in a burner with a daily capacity of 25 tons of C<sub>1</sub>H<sub>2</sub>. The hydrocarbons are intimately mixed with oxygen in the burner and made to react by igniting. It is impossible to prevent the formation of soot in the flame. In order to prevent the acetylene, formed in a reaction period of a few milliseconds, from decomposing again into soot and hydrogen or from reacting with steam to yield CO + H<sub>5</sub> the cracked gases are quenched by injecting a cooling agent. Two means of quenching are available. First, water may be employed. This gives rise to sooty water from which the soot can be separated by floatation and then disposed of by burning. Soot still

## TABLE 2

For each 100 kg of pure acetylene are required:

200 hg hydrosarbons

- ,000 LWh for the electric an
- 250 kWh power for the resovery of desired gases. 150 kg steam

The following hy-products are obtained:

- 49.5 hg C.H.
- 29 bg earbon black
- 15 bg residual all
- 200 set hydrogen

remaining in the gas can be removed by means of a filter. Plants erected in many countries operate on this principle.

The other means of quenching has been recently developed. It consists of injecting a thermally stable, preferably aromatic, hydrocarbon oil into the flame. The heat that the oil removes from the gases is exploited in a wasteheat boiler. About 95 per cent of the carbon black is recovered by this means. The remainder is removed in a column in which the heavy vapours of the quenching oil condense at the same time. The oil will tolerate 25 to 30 per cent of carbon black without difficulty. In order to ensure that this concentration is not exceeded, part of the soot-laden oil can be continuously drawn off and replaced by fresh. The oil containing carbon black is too valuable for heating purposes, and can be regenerated by evaporation at about 500°C. The acetylene carbon black consolidates to form a hard, abrasion-resistant petroleum coke, an excess of which is drawn off.

The cracked gas is compressed in order to allow recovery of the acetylene. It is then treated with N-methylpyrrolidone, which is a selective solvent for acetylene. If water is used for quenching, naphthalene and its homologues are present in the cracked gas, and these must be removed in a pressureless scrubber before compression takes place. If oil is used for quenching, the naphthalone is concontrated on an intermediate tray in the oil column, where it is drawn off. In this case, the scrubber is installed after the compressor. The scrubbing modium is the solvent from the main scrubber. It no longer extracts naphthalene but the very readily soluble homologues of acetylene. Consequently, in the following section of the plant, in which pure acetylene is obtained, polymerization and associated scale can no longer occur. This last section consists of an sbeorber, a rectifier and a degasifier. The gas is broken up into three fractions by lective solvent. The components that are less soluble . . than asstylene — particularly hydrogen, carbon mononide and methane — are separated in the absorber column. This fraction contains about 90 per cent of hydrogen and carbon monoxide, and can be readily processed to synthesis gas for the manufacture of ammonia or methanol. Acceptence of more than 99 per cent purity is drawn off from the restifier system. If a sulfur-free fedeteck has been used, no further treatment would be necessary for further proceeding the acetylone. Residual gas still sining asstylene is returned to the circuit in front to compressors. The activat is led over the degree in which the higher acetylenes are removed, and it is then recycled to the absorber.

The first industrial-scale acetylene plant of this description was taken on stream in Texas in 1952. The process has now become established throughout the whole world. To date, there are eleven units with a total capacity of 300,000 tons per annum in operation or in construction. They are erected by the Lurgi-Gesellschaft für Wärmetechnik mbH, Frankfurt/Main, and by the Chemical Construction Corporation, New York, under licence from the Badische Anilin- & Soda-Fabrik.

Tables 3 and 4 list raw material and energy consumption together with the by-products obtained if natural gas and light naphthu are used as feedstocks.

### 3. HTP process

In another process, the high-temperature pyrolysis process developed by Farbwerke Hoschet, the cracking temperature required for the formation of acetylene is again attained with the aid of a combustion reaction. Ethylene is obtained as well as acetylene in this process (6).

TABLE 3. MANUFACTURE OF ACETYLENE PROM NATURAL GAS BY THE BASE PROCESS

The data given n	olor to row mat	erials of the follow	ing composition :
Natural gas	Methane	95 per cent vol.	
Onygan:	O <sub>t</sub> content	96 per cent vol.	
	N <sub>1</sub> + argon	2 per cent vol.	
		Naphshalonr geonek 7.9 per sent Cylls in orached pas	Water quantit 8.4 per satt in crached par
Rev meterial	commption		
per kilogram e c'uood	€ C <sub>1</sub> N <sub>1</sub> pro-		
Natural ga	(without		
inerts) em	inding gas		
required fi	or the pro-		
heater		4.2 lig	4.1 kg
Окудая (епре			
100 per es	nt pure gas)	5.0 kg	4.9 kg
Yold of by-p Likeyram of duced			
Long gas.		10.0 m² 3TP	9.9 m² STP
Steam (60 pri	<b>a)</b>	1.5 hg	
Steam (30 p		4.7 bg	-
Potroloum or	<b>1</b>	0.13 hg	
Utilities per l C <sub>2</sub> II <sub>1</sub> produce	nd in the second second second second second second second second second second second second second second se		
	d by water	6.000 heat	14.000 hasi
Total dash	e e e e e e Mys e e e e	1.9 kWh	23 199
Pool voter f	er beiler for diluting	10.5 hg	-
bigher av	lylanan	6.2 m² 979	6.2 m² 877
	nagitalizatione .	6.65 m² 517	
New comm	n mption	e.del he	6.685 hg
Naghthalans		-	
		6.100 kg	
Light of on	numption.	0.016 hg	7.5 hn
a ann an ta	📫 i kara ka	-	1.8 Mg

Ì,

### TABLE 4. MANUFACTURE OF ACETYLENE PROM LIGHT NAPHTHA BY THE BASE PROCESS

Light napht	wt.	30-110°C aromatic scaffins + naphthan wt.	
Oxygan	O <sub>1</sub> content N <sub>1</sub> + argen	96 per cent vol. 2 per cent vol.	
		Naphshalone quanch 9.3 per april Call, in crached par	Water quanch 9.5 per sent C <sub>1</sub> II <sub>1</sub> in crashed per
	el consumption per of C <sub>2</sub> H <sub>2</sub> produced		
Light no		4.2 kg	4.1 hg
present	as the 100 per ure gau)	4.3 hg	4.2 hg
Yield of hy- gram of (	products par kilo- Cylly produced		
Lenn gn		8.4 mª STP	8.25 m² STP
Steam (		1.2 hg 4.0 hg	
Steam (3 Potroloui	n aaka	0.32 kg	
Unilinios p C <sub>2</sub> N <sub>2</sub> pr	or kilogram of oduori	,	
Heat re	moved by water	5,000 heel	12,090 incel
	petricity	2.6 kWh	2.0 kWh
Long gas	ter for boiler	6.8 m² 977	8.8 m² STP
higher	pa for diluting asstylenes	0.24 m² TTP	0.24 m² STP
	for regeneration	0.15 m² STP 0.005 hg	0.005 kg
	dans consumption		
Links of	ensumption .	0.014 hg	7.5 hm

try energy is The and on t her h na ha - in on t in the process d = e 16 د ما a per bus on period of about  $3 imes 10^{-6}$  set rind. After a re nd by a b e presidente e a are directly a at itself is form ac the are ie eil th us that prov 10.00 1005. This g nd fra r and m n ail is e 1 T for 1 n an Ì \* 1 t in s . .... harat. 1 8 1 a d nt e w part of di in ( ست النع ي . n. The li n aprivas as pal a **far** ii na io ao int ø ĝ had in the pr

The next stage is the compression of the cracked gases to about 210 paig and the removal of carbon dioxide by scrubbing with a potassium methyl taurinate solution. this is followed by recovery of higher acetylenes, which polymerize very readily, and higher hydrocarbons. The scrubbing modium in this case is the naphtha that is fed to the burner-reactor systems. As there is insufficient naphtha to allow scrubbing at normal temperatures, it must, like the cracked gases, be cooled to 30°C by means of a brine solution. The gas leaving the naphtha scrubber contains C<sub>2</sub> and C<sub>1</sub> hydrocarbons in addition to hydrogen and carbon monoxide. It is streamed to the acetone scrubber for the recovery of pure acetylene, a scrubber which operates at about 20°C and 170 psig. i'he acetyiene-free cracked gas is then compressed from 170 to 260 psia and separated into its components in a low-temperature distillation unit. The pure ethylene thus obtained can be further processed. The methane recovered may also be chemically treated or may be used together with the hydrogen fraction for producing energy for the HTP process. The same applies to the carbon monoxide fraction.

TABLE 5. HOBCHET HTP PROCESS Plant for 100,000 tone C<sub>1</sub> per annum (40,000 tone C<sub>2</sub>H<sub>3</sub> and 40,000 tone C<sub>2</sub>H<sub>3</sub>)

Capital costs DM 65 million (battery limits, including gas separation)

Materials commond for each 100 kg of C, produced

Fuel gas	0.66 million koal (self-produced)
Oxygen.	122 mº STP
KM tourinate (100 per cent)	0.4 kg
NaOH (22 per cent)	5.0 kg
Acetone	0.2 kg
Sait	2.0 kg
NH.	0.04 kg
Light nephthe.	192 kg
Utilities per 100 kg C1 produced	
Cooling water	25 ml

	3.5 MW
Food water for boiler.	0.2 m²
Steam (170 paig).	0.25 tons
Steam (40 paig)	Sulf-produced
Electricity	180 ÈWh
Air	3.2 m² \$TP
Nitrogan	Varying small amounts of nitro- gan for purging that starting

By-products

Residual gas	0.74 million heat (of which
	6.66 are required for produc-
	ing energy)
Created oil and light oil	20 hg
Ethane.	2 hg (non be recycled to the
	arealting unit)
Personal events	• ·

15 mm av shift

### Valation and

4 per cast of the capital casts

At present, Farbwerke Hoechst are producing 70,000 tons per annum of acetylene/ethylene with a very high degree of purity by this method. The total yield is high, being 53-54 per cent by weight for light naphtha feedstocks. Total heat requirements for cracking are met by burning the cracked gas. The only by-products obtained consist of about 10 per cent of cracked liquids (aromatic distillate and quenching oil), which are used as fuel for producing steam.

Capital costs for a plant producing 100,000 tons annually of  $C_3$  and the utilities for each 100 kg of  $C_3$  produced (40 kg  $C_3H_3 + 60$  kg  $C_3H_4$ ) are listed in table 5.

### III. PRODUCTION OF ETHYLENE

1. Autothermic cracking of crude oil in fluidized beds

The BASF ethylene process yields ethylene and other olefins from crude oil (7). No pretreatment of the crude is necessary. Heavy oil residues and sulfurous crudes may also be used as feedstocks.

Preheated crude or residue oil is injected into a fluidized bed consisting of grains of petroleum coke. The gas used for fluidizing the bed comprises a preheated mixture of steam and oxygen. At the temperatures involved, steam may be regarded as an inert gas, but oxygen reacts with the coke to form carbon monoxide and carbon dioxide. The heat thus given off raises the temperature of the mixture of steam and oxygen and of the injected oil to about 730°C, and thus meets the thermal requirements for the cracking reaction. The carbon formed by this means is deposited on the grains of coke in the fluidized bed.

The gases and vapours formed in the reaction pass through a cyclone, in which the particles of coke carried over from the fluidized bed are removed and returned to the reactor. In a subsequent quencher, the products of reaction are cooled to about 300°C by oil produced during the cracking process. The heavy oil fraction condensed by this means is recycled to the fluidized bed and carbonized, supplying the petroleum coke for combustise with oxygen. Excess coke is removed from the fluidized bed.

Most of the heat of the mixture of gas and steam that enters the lower part of a fractionating column at 300°C is imparted to a waste heat boiler for generating steam. A medium oil fraction condenses in the upper part of the column, where it is drawn off as a useful by-product. The temperature at the head of the column is about 110°C.

The mixture of gas and steam is then passed through a direct cooler in which steam from the fluidized bed and light oil vapours are condensed. The cracked gas leaves the cooler at almost the same temperature as that of the cooling water. Light oil and water are removed in a separator. The water is passed through a tube cooler, and pumped back to the head of the direct cooler, while the light oil is conveyed as a phlegmatizing agent to the top of the fractionating column. The excess removed represents a useful by-product.

# TABLE 6. AUTOTHEBASIC CRACKING OF CRUDE OIL BY THE BASIF PROCESS

Consumption figures and yield of by-products

------

No. of Concession, Name

k

	Ndinas ( Sumatra)	Sulti- Johra (Likya)	Massi- ideoscend (Saharo)	Burek
r each ten of ethylene are required				
Crude oil, kg	4,596	5,102	4,820	6,682
Onygen 96 per cent, mª STP	1,149	1,299	1,236	1,841
Nitrogen, m <sup>2</sup> STP	55	55	55	55
Compressed air for process control, m <sup>1</sup> STP	13	13	13	13
Feed water for boiler, kg	4,667	5,104	4,890	6,261
Electricity, kWh	160	178	168	233
Cooling water, m <sup>2</sup>	93	109	1)0	125
Fusi oil, ig	75.3	83.6	<b>\$</b> 0	110
p-products per ton of ethylene produced				
Gaseous (CO, free), mº STP.	2,206.4	2,841.4	2,555.1	3,185
H. kg	40.0	56.5	56.0	47.
N <sub>b</sub> , kg	72.7	85.5	81.4	129
CO, kg	440.8	530.3	515.1	734
Clinks	638.1	783.7	615.0	
	4.5	10.6	5.0	6
	206.0	226.5	215.4	240
	501.9	582.1	529.3	814
	22.9	35.8	25.6	39
	121.4	131.8	125.6	200
С.н	106.6	136.8	130.3	227
	10.0	11.9	11.1	21
Liquid				
Minture of aromatics, kg	714	849	771	1,17
Henvy aromatim, kg	217.5	246	231	541
Solid				<b>.</b>
Petroloum coke, kg	206	214	193	421
Energy		3, <b>520</b>	3,350	4.29

TABLE 7. CANTAL COSTS FOR THE PRODUCTION OF 60,000 TONS OF ETHYLENE PER ANNUM BY THE BARF AUTOTHERMIC CRUDE OIL CRACKING PROCESS FOR DEPRENT CRUDE OILS

	Sumatra : Minas	Libers: Babi-Delre Salare : Massi- Messarut	Euroit
	DM.	DM	DM
(1) Equipment and machinery	3,771, <b>80</b> 0	4,080,000	4,390,000
(2) Pipelines and fittings	1,500,000	1,606,000	1,814,000
(3) Presses control equipment.	500,000	520,000	545,000
(4) Service equipment, installation of buildings, electrical installation	<b>690,000</b>	718,000	753,000
(5) Brestion costs for the production unit	1,441,700	1,542,000	1,773,090
(9) Eiven work and steel framework	1,635,500	1,766,000	1,933,000
(1) Insulation and pointing	\$85,900	632,900	696,000
	10,124,900	10,864,580	12,104,099

300

As already stated, almost any crude oil may be used as feedutock. Consumption figures for feedetocks, auxiliarise, and utilities and the yield of by-products for each ton of ethylene produced are given in table 6 for four different crude oils. It can be seen that the paraffinic Minas crude gives the best yield. The largest amounts of feedetock are required for the Kuwait crude, which also gives rise to the largest yield of by-products.

Capital costs for plants producing 60,000 tons of ethylene annually from these crude oils are listed in table 7. It can be seen that the Kuwait crude incurs the greatest capital costs. The figures listed must be increased by about 10-15 per cent to allow for present-day conditions in the Federal Republic of Germany. In addition, the charges for the low-temperature separator would have to be included. The cost of an oxygen plant has also been omitted.

IV. RECOVERY OF MONO-OLEFINE FROM MEXTURES OF GASES AND PURIFICATION OF OLEFIN PRACTIONS BY SELECTIVE HYDROGENATION

# 1. Recovery of mono-olefins with the aid of metallic salt solutions

In general the recovery and concentration of olefins present in mixtures of cracked gases are effected by distillution and physical scrubbing processes using hydrocarbons or other suitable solvents. Chemical scrubbing techniques have been developed for special purposes; an interesting example of this is the separation of olefins from parafins and other inert gases by means of metallic salt solutions (8). The underlying principle is that olefins tend to form reversible chemical compounds with metallic salts. The scrubbing media employed are solutions of silver fluoborate or ethanolamine cuprous nitrate. They differ from one another in respect of their selectivity and capacity for olefins

To elucidate the following tables it may be said that absorption was carried out at elevated pressures and denorption at reduced pressure. The equipment consists of one absorption and several desorption towers. Between them an intermediate flash-column is installed in which small amounts of gas, most of which is physically dissolved, are flashed off and returned via the compressor to the scrubbing process. Acetylene, which forms acetylides with both silver and cuprous salts, must be removed before the gases enter the scrubber; for example, by selective hydrogenation.

Operational data, including amounts of gas and analytical results, on an industrial-scale plant for sepurating olefins with cuprous salt solutions are listed in table 8. The plant is on stream in Farbwerke Hoechst, Gendorf.

Further processing depends on the application for which the olefins are intended. As the  $C_3H_3$  and  $C_3H_6$ olefins are to be highly concentrated, they can be separated by low-temperature distillation. It has been proved that the above scrubbing process together with lowtemperature distillation of the olefin concentrate is just as economical as distillation of the whole gaseous mixture.

# TABLE 8. RECOVERY OF MOND-OLEFINE BY MEANS OF METALLIC SALT SOLUTIONS Operating data for the Gendorf plant

Presente		Tengermure
Absorber	110 17	Absorber         20°C           Intermediate flash off         20°C           Desorbers I and II         50°C           Cracked gas to the absorber (m <sup>8</sup> /hr)         3,500           Caprous salt solution (m <sup>8</sup> /hr)         120

### Amounts of gas and analytical data

		lar -	Juser . Ann	nadiate k aff	Restit	ual par	Olefin per		
	nt STP/ hour	per cent vol.	nt STPi hour	per cent vel.	nt STP/ hour	per cant vol.	m" STPi hour	par cali vol.	
H	678	19.4	8	20	665	38.7	5	0.3	
<b>œ</b>	95	2.7	1	2	_		94	5.4	
СН	949	27.1	19	48	<b>92</b> 1	53.5	9	0.5	
СН	119	3.4	2	5	112	6.5	5	0.3	
С.Н.	1.519	43.4	7	18	5	0.3	1,507	86.6	
С.Н	3	0.1			3	0.2			
Сн	137	3.9	3	7	14	0.8	120	6.9	
	3,500	108.0	40	100.0	1,720	100.0	1,740	100.0	

# TABLE 9 RECOVERY OF MONO-OLEFING BY MEANS OF METALLIC SALT VOLUTIONS

Cuprous sait solution process

Annual capacity Capital costs	15,000 tons of ethylene DM 2,500,000 (barrery limit)
Utilities (cracked gas not compre	mond) for each 100 kg $C_{\rm B}H_{\rm 4}$ pro-
duod Electricity Cooling water Hot water (90°C) Air	28 kWh 15 m <sup>a</sup> 3.3 m <sup>a</sup> 0.5 m <sup>a</sup>
Chemicals consumed for each 10	0 kg CyH4 produced
Copper solution, fresh	0.05 kg
Copper solution, regenerated	0.28 kg
Mongethanolamine, crude	0.12 kg
NaOH (100 per cent)	1.10 kg
Sulfuric acid (96 per cent)	0.10 kg
Silver solt a	plution process
Canital costs	DM 2,900,000 (battery limit

**Capital** costs Utilities (cracked gas not compressed) for each 100 kg CaHe produced 47.3 kWh Electricity 10.0 m<sup>3</sup> Cooling water lá kg High pressure steam. 3,800 cal . . . . . . . . Cooling oils Chemicals consumed for each 100 kg CsH4 produced and a second second 0.5 m<sup>8</sup>/year Silver salt solution (losses) 2 m<sup>2</sup>/year Silver sait solution for recovery

The consumption figures for utilities and raw materials required for each 100 kg of ethylene produced and the capital costs for a plant with an annual capacity of 15,000 tons of ethylene are listed in table 9.

The cuprous salt process is suitable for the initial concentration of ethylene and propylene from dilute cracked gases. The silver salt process should be employed for recovering ethylene of 99.9 per cent purity from waste gases with a high ethylene concentration but containing no propylene.

Scrubbing with metallic salt solutions is eminently suitable for small units, particularly if separation of paraffinic gases into individual fractions is to be dispensed with. It is also suitable for the recovery of olefins from refinery gases and residual gases obtained in olefin processing, which often contain olefins in low and varying concentrations.

# 2. Purification of olefin fractions by selective hydrogenation

The by-products obtained in the production of ethylene by the pyrolysis of hydrocarbons are olefin-rich fractions which, themselves, may be used as petrochemical raw materials. However, if they are to be put to this purpose, undesirable impurities must be removed. This can be successfully accomplished in practice by the selective low-temperature hydrogenation process developed by Farbenfabriken Bayer AG, Leverkusen (9). In this

process, hydrocarbon feedstocks are refined in the liquid phase (spray phase) at normal or slightly elevated temperatures over fixed beds of catalysts and with hydrogen under pressure. The throughput is high.

Thus, methylacetylene and propudiene can be removed by selective hydrogenation from propylene fractions, the amount of propylene itself being unaffected. In a similar manner, C4 acetylenes can be removed from C4 fractions. A variation of the process can be used to remove residual butadiene from C4 streams. Owing to the fact that hydrogenation takes place in the liquid phase, the feedstocks concerned, which are usually liquid, can be directly hydrogenated without being vaporized. In view of the low hydrogenation temperatures and the peculiar properties of the special catalysts, no polymerization takes place, with the result that no redistillation or after-treatment of the hydrogenated products is required. The catalyst has a very long life. Very high throughputs are feasible. For example, 10-30 kg of Ca and C4 fractions can be hydrogenated per hour per litre of catalyst volume. Accordingly, the reactors are comparatively small. For instance, a catalyst space of only 250 litres is required for the hydrogenation of 40,000 tons of C<sub>8</sub> fractions per annum. Furthermore, the space velocity can be varied within wide limits without the results being affected. However the hydrogen must be free from catalyst poisons.

Pyrolysis crack gasolines are obtained in the production of gaseous olefins from liquid hydrocarbons. These, too, may be refined by hydrogenation at temperatures of less than 100-C. The product obtained is an ageingresistant gasoline with the same octane number as the feedstock.

TABLE 10. SELECTIVE HYDROGENATION OF A C. FRACTION

Temperature at the catalyst		•				•		10-20°C
Pressure in the reaction chamber.	•	•	•	•	·	·	·	210 paig (max.)
Space velocity, kg/1 hr			•	•	•	•	•	20

Analysis before and after hydrogenation

Com <b>ponent</b>	Judet parts by weight	Outlet parts by weight
Ethane	5.7	5.9
Propane	43.3	50.7
Ethylene .	0.3	0.05
•	937.5	944.5
Propylene	5.4	< 20 ppm
Aliene	7.4	< 10 ppm
Methylacetylene.	0.2	0.1
Cyclopropane.	0.4	
-	1.000.0	1,001.05

Feedstock: 100,000 tons of C<sub>s</sub> fractions from the pyrolysis plant per annum

Utilities:

C villings .										and all OTR/ba
H <sub>s</sub> (70 per cent)	,	•	•	•	٠	٠	٠	•	•	500 m 51r/nr
Refrigeration energy (0°C)								•	•	360,000 KOM/TIT.
Blectricity			•		٠	•	•	•	٠	45 kWh/hr.
Capital costs: DM 600,000										

TABLE 11 SOLICTIVE HYDROGONATION OF A C4 PRACTION

Foodstock	
100,000 tons of C <sub>4</sub> fractions per annun (30-40 per cent of butadiens, 1,300 400 ppm of ethylacetylens)	
Temperature at the catalyst	10-20°C
Pressure in the reaction chamber	LIO pig (max.)
Space velocity, kg/1 hr	20
Butadione recovered	96 per cent wt
Residual vinylacetylene.	90 ppm
Residual ethylacetylene	1.90 ppm
Utilities .	
H <sub>a</sub> (70 per cent)	180 m³ STP/hr
Refrigeration energy (0°C)	240,000 kcal/hr
Electricity	38 kWh/hr
Capital costs DM 580,000	

Results of hydrogenating  $C_5$  and  $C_4$  fractions are given in tables 10 and 11. Figures are also quoted for capital costs and consumption.

### V. PROCESSING OF C4 FRACTIONS AND RECOVERY OF PURE BUTADIENE

### 1. Extraction of butadiene from C<sub>4</sub> fractions by means of N-methylpyrrolidone

This BASF process allows butadiene with a very high degree of purity to be extracted in one operation from crude  $C_4$  fractions containing socylene and allenes (10).

It is essentially a separating process employing N-methylpyrrolidone as the selective solvent. The crude C. mixture is evaporated and scrubbed with a side stream of N-methylpyrrolidone, which dissolves the acctylenes contained in the C4 mixture. The acetylenes are stripped with steam in the lower part of the scrubber. The C. stream thus partially purified is then scrubbed with the bulk of the N-methylpyrrolidone in the main tower. The solvent removes all the butadiene and part of the butenes from the ascending gases. The butylene fraction is collected at the head of the scrubber, and is liquefied by cooling with water. The solvent charged with butadiene and butenes is passed through a rectifying section, in which an ascending current of pure gaseous butadiene strips the less soluble butenes from the descending spray of solvent. The strip-gases, consisting of butadiene and butenes, are recycled to the main-scrubber. Pure butadiene is collected in the lower part of this countercurrent stripper. It is washed with N-methylpyrrolidone and water, and finally liquefied. The solvent is returned to a boiler, where it is freed from dissolved gases and excess steam.

The extremely high selectivity of the solvent allows butadiene of 99.5-99.8 per cent purity to be recovered, the yield being of the order of 98 per cent. If an even higher degree of purity is desired, the butadiene drawn off from the counter-current stripper should be led over another scrubber column. Here the residual acetylenes and allenes are removed from the butadiene by means of a side stream of degasified solvent. The impurities, strongly diluted with steam, are ied off through a side outlet. A feature of the separating process is that the costs are very low, especially heating and electricity charges. The consumption of solvent is negligible

Capital costs for a plant producing 24,000 tons of butadiene annually and the corresponding consumption figures are listed in table [2.

# 2. Separation of isobutylene from butene fractions

After the removal of butadiene from gaseous olefins obtained by the pyrolysis of liquid hydrocarbons, there remains a C<sub>4</sub> mixture that contains approximately equal parts of isobutene and normal butene. Butadiene can be formed by dehydrogenation of normal batene, but first of all the isobutene must be removed from the fraction. A market should then be available for the isobutene. but this is not usually the case. Thus, it is advisable to convert the isobutene to such products, a market for which can always be found. Bayer's D.I.B. process provides an interesting means of doing so. In the presence of certain solid catalysts, the isobutene can be almost completely converted to a mixture of dissobutylene and triisobutylene. This mixture can be readily separated from the normal butenes by distillation, with the result that normal butenes more or less free from isobutenes are available for chemical processing. The liquid products recovered (isooctene and isododecene) are extremely pure and are capable of increasing the octane number of automobile gasolines. If desired, the isooctenes can be converted into alcohols for plasticizers by the oxo process.

Figures for the yields, utilities and capital costs entailed in processing 100,000 tons annually of a butadiene-free  $C_4$  fraction containing 45 per cent isobutylene are listed in table 13.

### VI. MANUFACTURE OF INTERMEDIATES

### 1. Production of acetaldehyde from ethylene by the Wacker-Hoechst process

As a result of the considerable increase in the production of ethylene, interest has been focused on the manufacture of acetaldehyde from ethylene. Technolo-

TABLE 12. NMP process for extracting butadiene from  $C_4$  fractions

• •	24,000 tons of butadiene $C_4$ mixture derived from the pyrolysis of light naphtha and containing 36-40 per cent of butadiene
Purity of the butadiene .	GRS quality (even higher purity may be obtained, e.g., poly-cis quality)
Capital costs	DM 6,000,000
Utilities per 100 kg of butadiene produced.	200 kg of steam 22 kWh 0.1 kg of NMP (max.)

TABLE 13. D.1 B. PROCEDB (FARDENFADRIKEN BAYER AG, LEVERKUSEN)

### F**eeds**tock

100,000 tons of C4 fractions annually free from butadiens and containing 45 per cent isobuitylene.

### Yield

110 parts yield 60 per cent dissobutviene and 40 per cent trisobutylene, including small amounts of higher butenes.

Utilities	
Steam Elactricity Cooling water	6.0 10ns/hr 200 kWh/hr 600 m <sup>a</sup> /hr
Capital costs	

DM 12,000,000

gical and economical considerations indicated that direct oxidation would be preferable to the process via the alcohol. The feasibility of the direct method was demonstrated in the laboratories of the Konsortium für elektro-chemische Industrie in Munich. Wacker Chemie, Konsortium, and Hoechst were responsible f: translating the results of these experiments into an industrial scale. Two variations have been worked out: the one a singlephase direct oxidation using oxygen, and the other a two-stage direct oxidation employing air.

The following description of the process has been taken from a publication issued by Aldehyde GmbH, Munich, who license the process.

The reactions involved in the direct oxidation of ethylene to acetaldehyde are described by the equations in table 14.

The catalyst, an aqueous solution of copper chloride with small amounts of PdCl<sub>2</sub>, serves as an oxygen carrier, and effects selective conversion of the olefin to the carbonyl compound. The reaction indicated by equation 1 takes place in a number of steps. A good idea of the reactions taking place in practice is obtained from equations 2 and 3. Ethylene and the aqueous solution of cupric chloride react in the presence of PdCl<sub>2</sub> to form acetaldehyde (equation 2). The cuprous chloride and hydrochloric acid that are also produced can be oxidized to yield cupric chloride and water once again (equation 3). This completes the cycle, and thus allows the process to be carried out continuously. The reaction and regene-

TABLE 14. ACETALDEHYDE PROCESS (WACKER-HOECHET)

	$C_{s}H_{4} + 1/2 O_{3} \xrightarrow{Catalyst} CH_{0}CHO' \Delta H - 52 kcal$
(2)	$C_{g}H_{g} + 2 CuCl_{g} + H_{g}O \xrightarrow{PdCl_{g}} CH_{g}CHO + 2 HCl + 2 CuCl$ (reaction)
(3)	$2 \text{ CuCl} + 2 \text{ HCl} + 1/2 \text{ O}_{1} \rightarrow 2 \text{ CuCl}_{0} + \text{H}_{0} \text{O} \text{ (regeneration)}$

ration mechanisms described by equations 2 and 3 may take place simultaneously, or separately.

# (a) Direct oxidation, single-stage with oxygen

Ethylene, oxygen, and recycle gas are led into a reactor filled with catalyst solution. The reaction takes place at slightly elevated pressure and at the corresponding boiling temperature of water the heat of reaction is drawn off by the evaporation of water, and the concentration of the catalyst solution is kept constant by commensurate water additions. The acetaldehyde is removed from the mixture of gases and vapours leaving the reactor by scrubbing with water. Apart from unconcerted ethylene, the aldehyde-free gas contains some oxygen, and its composition is checked by instruments. It then returns through a compressor to the reactor.

In order to maintain the proportion of inert gases recycled at a constant level, a side stream is bled off to another reactor for further conversion. The constituent ethylene is almost completely converted after the addition of oxygen.

# (b) Direct oxidation, two-stage with air

Ethylene is almost completely converted by passing it once through a flow reactor at moderate pressures and average temperatures. The heat of reaction is imparted to the catalyst solution in the reactor, and serves to distil off the acetaldehyde in the subsequent flash chamber. The acetaldehyde is then concentrated by dephlegmatization. The catalyst solution freed from aldehyde is pumped into another reactor, where it is oxidized with air, after which it is streamed back into the reactor, where the ethylene reaction takes place.

The fact that conversion takes place in two separate reactors and that a gas cycle has been renounced allows ethylene-rich gas mixtures to be used instead of pure ethylene. Oxygen is consumed to such an extent that the spent air may be used as protective gas. The twostage process can also be run on oxygen if it were available at a low price.

# (c) Recovery of the crude acetaldehyde

The crude acetaldehyde obtained in either of the above processes is separated from water and highboiling fractions in a distillation column, and subsequently degassed. The purified product is of comparable quality to acetaldehyde derived from other processes.

In order to provide a comparison of the economics of the two processes, estimated capital costs and consumption figures for plants of 15,000, 30,000, and 60,000 tons annual capacity are given in tables 15-17. The basic assumptions are that ethylene of at least 99 per cent purity is available at 90-170 psig in the vicinity of the plant and that facilities already exist for oxygen for the single-stage process. In other words, no new facilities need be provided for ethylene and oxygen.

The figures from which the capital costs (table 15) have been drawn up pertain to units that are currently on stream. They are based on labour and material costs in the Federal Republic of Germany.

# TABLE 15 PRODUCTION OF ACETALDOHYDE PROM ETHYLENE (WACKER-HORCHOT PROCESS)

Estimated capital costs including engineering

Capacity	Production will						
tona per annum	Single-stage with exygen	Two-stage with at					
	DM	DM					
15,000	5,500,000	6,700.000					
30,000	8,100 000	9.600.000					
60,000	11,700,000	14,900,000					

The capital costs cover production plant with all necessary equipment, all buildings and housing belonging to the production unit, all measuring and control facilities, switchgear, intermediate storage tanks, erection of the complete plant, initial charging of the reactor with catalyst solution, and total engineering costs.

Items that are not included in the capital costs are additional facilities such as large storage tanks, steamgenerating facilities, transformers, water treatment plant, land, and access roads. Consumption of materials and utilities are given in tables 16 and 17.

A decision as to which method should be preferred, i.e., direct oxidation single-stage with oxygen or direct oxidation two-stage with air, depends on local conditions such as the price of oxygen, the degree of purity of the ethylene, energy costs, etc.

These data have been derived from current production figures.

# 2. Direct oxidation of ethylene to ethylene oxide

The direct oxidation process which has largely superseded the classical chlorohydrin process, is very economical in view of the low current prices for ethylene. Although the plant costs are greater than those for the chlorohydrin process, the new direct oxidation process is more favourable in that it dispenses with a chlorine factory and the additional power installations involved.

### TABLE 16. PRODUCTION OF ACEIALDENYDE FROM ETHYL&NE (WACK&R-HORCHET PROCESS)

Materials, utilities, personnel, and maintenance costs

	Amounts for each 100 kg of acetablehyde produced			
	Single-singe with oxygen	Two-stage with air		
Materials				
Ethylens (90 or 170 psig, 99.7 °) Oxygen (90 psig, 99 %)	67 kg 29 m² STP	67 kg		
Hydrochloric acid + catalyst	DM 0.6	DM 1.2		
Utilities				
Cooling water. Artesian water (for further cool-	30 m <sup>a</sup>	20 m*		
ing)		1.5 m <sup>a</sup>		
Soft water for boilers	0.3 mª	0.02 m <sup>s</sup>		
Steam (180 psig)	0.13 ton	0.03 ton		
Steam (50 juig)	0.03 ton	0. <b>09</b> ton		
Electricity	21 kWh	37 kWh		
Personnel				
1 chemist, I foreman				
Workers (expressed in terms of amount of labour required to produce 100 kg)				
For 15,000 tons annually	0.192	0.192		
For 30,000 tons annually	0.096	0.096		
For 60,000 tons annually	0.048	0.048		

# TABLE 17. PRODUCTION OF ACETALDEHYDE FROM ETHYLENE (WACKER-HOECHST PROCESS)

(Plant operating for 8,000 hours per year)

	Capacity, tons per annum					
	15,000	30,000	<b>60,000</b>			
Direct oxidation, single-stage with oxygen						
Ethylene (90 paig, 99.7 per cent)         Oxygen (90 paig, 99 per cent)         Cooling water         Soft water for boilers         Steam (180 paig)         Steam (50 paig)         Electricity	1,005 m <sup>8</sup> STP 544 m <sup>8</sup> STP 575 m <sup>8</sup> 6 m <sup>8</sup> 2.5 tons 0.6 ton 400 kWh	2,010 m <sup>s</sup> STP 1,088 m <sup>s</sup> STP 1,150 m <sup>s</sup> 12 m <sup>s</sup> 4.9 tons 1.1 tons 800 kWh	4,020 m <sup>3</sup> STP 2,176 m <sup>3</sup> STP 2,300 m <sup>3</sup> 23 m <sup>3</sup> 9.8 tons 2.3 tons 1,600 kWh			
Direct oxidation, two-stage with air						
Ethylene (180 psig, 99.7 per cent). Cooling water . Artesian water for further cooling . Steam (180 psig) . Steam (50 psig) .	1,005 m <sup>a</sup> STP 375 m <sup>a</sup> 28 m <sup>a</sup> 0.6 ton 1.7 tons 780 kWh	2,010 m <sup>3</sup> STP 750 m <sup>3</sup> 55 m <sup>3</sup> 1.1 tons 3.4 tons 1.400 kWh	4,020 m <sup>2</sup> STP 1,500 m <sup>2</sup> 110 m <sup>2</sup> 2.3 tons 6.5 tons 2.600 kWh			

Another advantage of direct oxidation is that no undesirable by-products are obtained.

The process consists of passing ethylene and atmospheric oxygen in a suitable ratio under pressure over a silver catalyst located in the tubes of special contact furnaces. The silver catalyst consists of a suitable carrier on which amorphous silver has been deposited. The ethylene is converted in the contact furnaces at temperatures of between 200°C and 350°C. A cooling system is provided for the large amounts of heat given off. At this, the Hüls process avoids the use of a liquid medium around the tubes of the furnace, as it is employed in many analogous processes. Water is used instead. The steam thus generated is fed to the turbine driving the recycle gas compressor. The mixture of gases leaving the furnace contains ethylene oxide, carbon dioxide. and water, as well as some unconverted ethylene and oxygen. The ethylene oxide is removed from the gas by scrubbing with water under pressure. Air and ethylene are introduced into the the remainder of the gas mixture until the required concentration is again attained. The recycle gas compressor then returns the mixture to the furnace. In order to maintain the quantity of recycle gas constant, the nitrogen in the air employed is continuously removed as the oxygen is consumed. However, some ethylene is entrapped in the stream of waste nitrogen, and more air must therefore be added to ensure its exploitation. The resultant gas mixture is streamed through a furnace with a high capacity and then through a scrubber. In this manner ethylene oxide is also produced from the waste gases. More energy for driving the recycle gas compressor can be made available by allowing the stream of high-pressure waste gas to blow down to atmospheric pressure through a turbine.

Gas is removed from the water containing ethylene oxide that has been recovered in the main and side scrubbers, and is compressed for recycling. The aqueous solution of ethylene oxide is pumped into a distillation column. The ethylene oxide is distilled off by indirect steam heating, and then purified in the concentrating column. The water at the bottom of the distillation column no longer contains ethylene oxide, and is drawn off and recycled. Small amounts of carbon dioxide are still dissolved in the ethylene oxide obtained, and must be removed in a stripper. The ethylene oxide produced can then be run into tanks (spherical containers).

An automatic remote control system is operated from a central control board. Consumption figures for each 100 kg of ethylene oxide produced and capital costs for a plant of 60,000 tons annually are listed in table 18.

# 3. Oxidation of butane in the production of aliphatic acids and solvents (11)

The process consists of the oxidation of n-butane by compressed air, which may be enriched with oxygen. Oxidation takes place in reactors at pressures of 850-1,140 psi and temperatu as of 160-200°C. These temperatures and pressures exceed the critical values for n-butane, with the result that a solvent has to be employed for the butane. For this purpose raw materials formed in the oxidation reaction, usually acetic acid, are taken. TABLE 18. DIRECT OXIDATION OF ETHYLENE TO ETHYLENE OXIDE (HULS PROCESS)

### Input

Ethylene											108 kg
Compressed air	,				•	•		·	·	÷	7 <b>50 m³</b>

### **By-products**

Aqueous solution of ethylene glycol

About 10 kg of each 100 kg of ethylene oxide produced are hydrolyzed to ethylene glycols

Capital costs for a unit of 60,000 tons annual capacity are of the order of DM 58,000,000, including control panel and social facilities

The heat given off during the exothermic oxidation process is largely consumed in evaporating the liquid in the reactor and in heating up the cold recycled feed. The products of reaction leaving the reactor together with unconverted butane are liquefied in a multi-stage condensation system. The low temperatures required for this are attained by blowing down the waste gases in a turbine, and the energy thus produced is used for compressing the air. All the condensates are passed over a separator, being split up into the raw product and a butane phase, which is recycled to the oxidation reactor. The yield of acetic acid, formic acid, and ester and ketone by-products can be varied within wide limits by adjusting the process variables, i.e., the ratio of the reaction components, the amount of water in the reaction mixture, and the temperature and pressure.

The crude product obtained is recovered by multi-stage distillation. Acetaldehyde, methyl mormate, and butane are drawn off in the first stage, and returned to the oxidation reaction. The next stage consists of distilling off the solvent (mixture of esters and ketones) from the aqueous solution of crude acid. Subsequently, the solvents are separated by azeotropic distillation into two different blends. One of these consists of acetone and methyl acetate, and the other of methyl ethyl ketone and ethyl acetate. The crude acid is also dehydrated by azeotropic distillation. The same means, azeotropic distillation, is then employed for removing the formic acid, which is subsequently concentrated and purified in two other columns. Acetic acid is then distilled off, leaving behind propionic acid and other residues, from which the small amounts of propionic acid are recovered in a batch process.

Consumption figures for each 100 kg of acetic acid produced and capital costs for a plant with a capacity of 40,000 tons annually are listed in table 19.

# 4. Manufacture of alcohols and ketones from olefins

The Rheinpreussen process for producing alcohols and ketomes from olefins or fractions containing olefins has given good results. It consists of esterifying the olefins with sulphuric acid and of hydrolyzing the resultant esters with water. The secondary alcohols produced can be dehydrogenated to the corresponding ketones with the aid of a highly reactive catalyst with a long life. Suitable feedstocks are desulfurized refinery gas fractions, e.g., propane/propylene containing 30-90 per cent propylene and butane-butylene containing 30-90 per cent iso- and n-butylene. The main products obtained are iso-propyl alcohol and secondary butyl alcohol. By-products consist of disobutylene, triisobutylene, diisopropyl ether, disec-butyl ether and liquid gas with a low olefin content.

The process consists of esterifying liquid feedstocks under pressure at 40-60°C with 70-80 per cent sulfuric acid in a series of autoclaves. The olefins and the sulfuric acid are streamed in opposite directions through the autoclaves. Any isobutylene present is previously removed in the form of di- and triisobutylene by scrubbing with sulfuric acid. The remaining saturated hydrocarbons, propane and butane, are separated from the sulfuric acid containing esters, and leave the unit in the form of liquid gas. Ester from the first separator is mixed with water, and hydrolyzed with steam. The acid and alcohols obtained are separated in a distillation column. The dilute sulfuric acid is concentrated and re-used. The alcohol vapours leaving the distillation column are neutralized, dehydrated, and fractionated.

The liquid alcohols are heated in an evaporator to a temperature above their boiling point, and the vapours are passed through a heat exchanger into a tube-bundle reactor made of special steel. Here they are dehydrogenated to ketones at about 250°C with the aid of a special catalyst. The products of reaction are cooled to room temperatures by means of a heat exchanger and a water cooler, the greater part of the ketones formed being thus separated. The hydrogen still contains ketones and some unconverted alcohols in amounts corresponding to the partial vapour pressures. These remaining components are removed in a condenser at temperatures of down to -30°C. The hydrogen obtained is extremely pure. The crude products are processed to pure ketones by continuous distillation. Synthesis and recovery are fully automatic.

TABLE 19. MANUFACTURE OF ACETIC ACID BY OXIDATION OF N-BUTANE

The data set forth below refer to normal operating conditions leading to the production of 2,000 tons of acetic acid per month and 400 tons of mixed solvents.

Values for each 100 kg of acetic acid produced:

### Feedstock

### By-products

10 kg of solvent blend consisting of acetone and methyl acetate; 10 kg of solvent blend consisting of methyl ethyl ketone and ethyl acetate

9 kg of formic acid and propionic acid

Capital costs for a plant with a capacity of 40,000 tons per annum are of the order of DM 40,000,000 (estimated), including control panel and social facilities

### TABLE 20

A. HYDRATION OF OLFFINE TO ALCOHOLS Consumption figures excluding concentration of the sulfaric acid

	Per ton	produced of
•••	lsopropyi Alcohol	sec-bury alcohol
Propylene	0.78	
n-butylene		1.0
Steam (360 psig).	. 3	10
Steam (130 psig).		1-2
Cooling water, m <sup>3</sup>	45	90
Electricity .	110	400

### B. DEHYDROGENATION OF SECONDARY BUTANOL TO METHYL ETHYL, KETONE

For each ton of methyl ethyl ketone produced are required:

Secondary butanol							1.05-1.045 tons
Steam (130 psig)							
Steam (40 psig) .							
Electricity							
Cooling water	·		•				25-30 m <sup>a</sup>

Some consumption figures for the hydration of propylene and butylene are given in section A of table 20. The consumption figures for the dehydrogenation of secondary butanol are given in section B of the table.

The processes discussed have been developed in a country that was comparatively late in replacing coal on a large scale by petroleum for the production of basic materials for chemicals. It is realized that not all of these processes will be of interest to countries that are building up their petrochemical industry. The choice of a suitable process will always involve careful study of the raw material position and of the market prospects for the finished products, particularly as only large petrochemical processing units have proved to be economical.

### SELECTED PROCESSES FOR THE PRODUCTION OF BASIC CHEMICALS AND INTERMEDIATES FROM PETROLEUM HYDROCARBONS

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# **B.** Nitrogenous fortilizers

# INTRODUCTORY SUMMARY

In this chapter, various aspects of the world production and consumption of nitrogenous fertilizers are presented. The prospects for the economical establishment of fertilizer manufacturing concerns in developing countries are also indicated.

At present, the production and consumption of nitrogenous fertilizers are heavily concentrated in industrialized countries. Europe and North America are not only the largest consumers but also the net exporters. Latin America is a budding net exporter, but Africa, Asia and Oceania are not importers. It is expected that with greater appreciation by the local farmers of the yieldboosting effect of nitrogenous fertilizers on crops, the highest rate of growth of fertilizer consumption will take place in developing countries. It would be necessary, not only to demonstrate to the farmers that fertilizers can increase the physical yield of crops, but also to make the commercial profitability of their use apparent.

Of the three main types of chemical fertilizers, namely, nitrogenous, phosphate and potassium, nitrogenous fertilizers are showing the greatest rate of growth in their agricultural use mainly because crops are apparently more responsive to their application. Nitrogenous fertilizers are produced from ammonia, hence there is a great deal of interest currently centred on the prospects for the production of synthetic ammonia from local natural gas or petroleum feed-stock.

Nitrogenous fertilizers are of several types, namely, ammonium sulfate, ammonium nitrate and urea. A reaction of ammonia with sulfuric acid, or with nitric acid or with carbon dioxide, yields respectively, ammonium sulfate, ammonium nitrate and urea. The production of ammonia is effected by a reaction of three units of nitrogen with one unit of hydrogen. The distinction between the various nitrogenous fertilizers is made on the basis of their relative contents of nitrogen as follows: 35 per cent of ammonium nitrate (and lined ammonium

nitrate). 25 per cent of ammonium sulfate and nitrosulfate and 8 per cent of urea. Anhydrous ammonia contains 83 per cent nitrogen and has the adva.its ge of being capable of direct application to the soil, that is, without the necessity of transforming it into the conventional fertilizer forms.

The above account puts synthetic ammonia in the centre of the production stage as the main intermediate raw material for the manufacture of fertilizers. A contemplation of the fertilizer industry is, therefore, often taken up with consideration about the feasibility of setting up ammonia plants.

The crucial question that arises is whether an ammonia plant should be based on the availability of natural gas or petroleum feed-stock. Petroleum-based ammonia has proved more economical than the coal-based ammonia, but it is not yet finally established which of the other two ways of producing ammonia would be more econoinical, namely, by naphtha or by natural gas. It is currently estimated, however, that the cost of manufacturing ammonia by naphtha is more expensive than by natural gas, but this estimate is done for different locations and different raw material endowments. With a continuing decline in the price of naphtha occasioned by the increasing refinery operations in most countries, naphtha may become the less expensive intermediate for the production of ammonia. In addition to the idea of setting up ammonia plants in developing countries, it is suggested that increasing improvements being made in the transportability of ammonia from distant places might make setting up plants to manufacture ammonia derivatives more preferable than setting up ammonia plants.

In general, the total cost of manufacturing ammonia as a base for the fertilizer industry should be considered in the context of the effects of such factors as size of plant, the raw materials to be used (naphtha or natural gas), electric power costs, actual location of plant, and the cost and skill requirements of the labour force.

# 1. THE PETROCHEMICAL INDUSTRIES Production of nitrogenous fortilinors

Propared for the United Natione Centre for Industrial Development by the Institut français du pétrole

### I. Ammonia production

### A. AMMONIA FEED-STOCKS

Since the Second World War feed-stocks for ammonia production have completely changed. Before the Second World War, 90 per cent of world ammonia was based on coal with most of the other 10 per cent based on electrolytic hydrogen. Since the lowest cost hydrogen will be used in any given plant and area, there has been a gradual change to natural gas and petroleum as a hydrogen source, so that today about one-third of total world ammonia production is based on coal sources and by 1975 this figure should decline to less than 10 per cent.

Coal is used in those countries that have large coal industries, such as the Federal Republic of Germany, France, Belgium, the Netherlands and esstern Europe; however, the trend in these countries is to petroleum and natural gas: England, for instance, which has a large coal industry, has almost completely switched over from coal-based ammonia to ammonia plants based on the steam-reforming of naphtha.

### **B. AMMONIA MANUFACTURE**

### 1. Recent improvements

Many improvements in the manufacture of ammonie have helped to reduce the high investment costs and accordingly the cost of production, and the stability of the price of ammonia, in spite of rises in raw material and labour costs, can to a large extent be attributed to the advancement of technology during the past ten years.

(a) Improvements in technology. There have been relatively few advances in the ammonia-plant synthesis section, but the synthesis gas-preparation section has had several important changes, such as:

- (i) Higher reforming pressures and improved catalysts;
- (ii) Improved CO shift conversion catalysts;
- (iii) Improved amine and hot potassium carbonate processes for removing CO<sub>3</sub>;
- (iv) Use of liquid hydrocarbons as raw material.

(b) Transport, storage. New developments in the storage and transport of ammonia have accompanied the growth in production:

(i) Refrigerated vessels up to 15,000 tons can now be built;

(ii) Storage at atmospheric pressure has improved the economics of this operation.

As a result, ammonia is on the point of becoming a commodity capable of being transported economically from the cheapest source of production to a market.

(c) Large capacity plants. Based on low-cost feedstock, a prerequisite to these giant projects, the economics resulting from size and new process technology are setting a new competitive standard of ammonia costs. The outstanding development: are the projects of the Olin Corporation and U.S. Stee Corporation, as both companies are planning to build large capacity plants at a single location (1,400 short tons/day two-train ammonia plant). These projects strengthen the trend set by the American Oil Company at Texas City, where a 210,000 short tons/year NH<sub>2</sub> plant came on stream last December, and by the Trinidad project of W. R. Grace and Co., which is now on stream.

The entry of oil companies into the fertilizer industry, with the primary objective of enhancing the end value of the crude oil barrel by integrating ammonia manufacture with their oil refinery operation, will no doubt result in ammonia projects on a similar scale as the cil industry's petrochemical plants.

(d) Competition. Against the economics resulting from the concentration of large ammonia capacity in a single plant with or without processing facilities into nitrogenous fertilizers and other products, the product distribution costs of large plants are likely to be proportionally higher than those of smaller capacity plants.

Efficient plants with captive markets, within an economic radius, are therefore likely to withstand the competition from the new giants, although inevitably the smaller uneconomic plants will become the victims. Growth of regional demand will increasingly govern and transport will circumscribe the impact of new competition.

An inevitable result, favoured by the lower investment costs attaching to the new plants and processes and the significant reduction in production costs, is expected to be the reduction of the cost of nitrogen to the farmer, esp.cially in developing countries where at present it is generally disproportionately high.

### 2. Ammonia processes

(a) Synthesis gas. There are two major processes for making synthesis gas from hydrocarbon feed-stocks:

steam-reforming of hydrocarbons and partial oxidation of hydrocarbons.

The principal disadvantage of the partial oxidation process has been the necessity of an air separation plant to produce the oxygen needed for the process. In cases where natural gas is the feed-stock, the additional cost of the air separation plant, together with its maintenance and safety problems, has been a limiting factor for the partial oxidation process. In these cases, the investment cost for a partial oxidation plant is approximately higher than the gas reforming route by the cost of the air separation facility.

During the past two years the steam naphtha reforming process developed by the Imperial Chemical Industries (ICI) has changed the complexion of new ammonia plants outside the USA. The naphtha feed-stock is a surplus refinery product available at a low price. No oxygen plant is required and since this new process has lower investment and operating cost than the partial oxidation alternate, it could displace the latter as a basic route for ammonia production in many countries where naphtha is in excess supply.

(b) Gas purification processes. The developments of new catalysts in CO conversion and the replacement in several new plants of the traditional two-stage CO conversion step with two  $CO_8$  removal units by a single CO unit using two catalyst beds with interquench and one  $CO_8$  removal unit, resulted in considerable savings in investment utilities.

On another side, because of the higher activity CO catalyst, the CO content of the gas entering the final clean-up stage fell from 3 per cent to 0.6 per cent. Since the MEA system yields lower exit CO<sub>3</sub>, this innovation has made the MEA system preferable to the hot carbonate system for CO<sub>3</sub> removal.

(c) Carbon dioxide removal. Final clean-up of synthesis gas to remove CO and CO<sub>1</sub> to less than 10 ppm is now accomplished by methanation instead of the conventional copper-liquor process, because of its lower investment, negligible operating cost and simplicity of operation.

(d) Ammonia synthesis. Although no new process has been introduced for ammonia synthesis in the last ten years, the trend has been towards adoption of the moderate pressure processes operating at 300 to 350 atm. The only improvements are:

- (i) The introduction of a new catalyst;
- (ii) The changes in the mechanical design of the converter, which result in better steam economy;
- (iii) The use of a steam-recovery system to utilize the heat of  $\pm$  product gas;
- (iv) The improvements in compressor design;
- (v) The size of the ammonia converters, which has increased from 120 tons/day prevailing in 1950 to 700 tons/day capacity.

### 3. Economics of ammonia production

The investment, material balances, utilities, catalyst and chemicals requirements are presented in table 1

### TABLE 1. 409 MT DAY AMMONIA PRODUCTION BY STEAM-REFORMING PROCESS (330 SED)

	<b>B</b> ars	ed 9
	Natural eas	Naphtha
Investment (Grass roots plant) mil-		
lions of dollars		
Process anits including paid-up		
royalties and initial catalysi		
and chemicals charges)	71	8.2
Off-sites (including utility genera-		
tion and refrigerated storage		
for anhydrous ammonia)	7.0	69
Start-up expenses	10	1.0
TOTAL	151	16.1
Raw material and utilities require-		
Natural gas * (m <sup>2</sup> /h))	23,709	
Naphtha <sup>p</sup> (rous/hr)	<b>a</b> ., <b>rub</b>	8.750
Fuel oil h (tons hr)		9,700
Treated water (m <sup>a</sup> /hr)	48	63
Chemicals and catalyst consumption		
(S/year).	52,500	158,000
Lubour (men/shift)	25	25
* Natural gas consumption is divided	as follows	nt' hr
Process requirements		10.300
Healing requiremonts		6,100
Electricity generation		7,300

LOTAL 23.700

<sup>9</sup> Naphtha is only used for process requirements. Fuel required for heating and electric power generation can be supplied by fuel oil or excess naphtha.

for a 400 tons/day ammonia plant erected in Europe or in the USA, using steam-reforming process and based, respectively, on natural gas and naphtha.

Tables 2 and 3 give the manufacturing cost and the derived selling price of ammonia produced, respectively, from natural gas and naphtha feed-stocks.

1. Effects of feed selection. Capital costs of naphthabased plants are 10 to 15 per cent higher than natural gas-based plants. Operating costs of a naphtha-based versus a natural gas-based plant depend upon the price of naphtha and natural gas. Figure I which illustrates

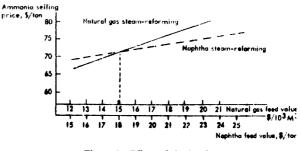
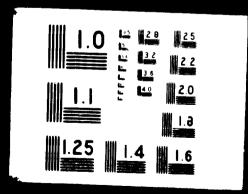


Figure 1. Effect of food value

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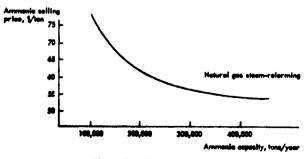
	Unit	Unit cost (\$US)	Annual quantity	Annal cor (10%/year)
Variable costs				
Raw materials and utilities				
Natural gas	10° m° m°	13 0.2	190,000 3 <b>84,</b> 000	2,470 77 52.5
Labour				34.3
Salaries and wages. Supervision at 25 per cent of	Men/year	5,000	100	500
salaries and wages				125
TOTAL VARIABLE COSTS				3,224.5
Fixed costs				
Depreciation	At 3.5	per cent of total per cent of total per cent of total per cent of total per cent of total	investment investment investment	
		Tor	L PIXED COFTS	3,490.0
Selling price		Manufa	CTURING CORT	6,714.5
Net cash flow at 20 per cent <sup>a</sup> of tota Depreciation provides		· · · · · · · · ·	· · · · · · · · ·	3,020 1,890 1,130 2,260 6,714.5
Ammonia sales		on)	· · · · · · · · ·	8,974.5 68

# TABLE 2. 400 MT/DAY AMMONIA PRODUCTION BY NATURAL GAS STEAN-REPORMING (330 SD) Manufacturing cost and ammonia selling price

· Return required for a five-year payout.

the effect of feed value on the ammonia selling price, shows that, based on current naphtha prices (\$18/ton), naphtha looks attractive, whereas natural gas is priced above  $$15-16/10^8 \text{ m}^8$ .

2. Effect of plant size. Ammonia plants with a capacity of about 200,000 to 400,000 tons/year are now planned in industrialized countries. The economics that such large plants have to offer are presented in figure II below.





The cost structure is based on a natural gas steamreforming plant.

In the USA, these large projects (1,000-1,200 MT/day) based on natural gas supplied at \$7/10<sup>9</sup> m<sup>8</sup>, will permit ammonia being produced at a cost price of \$35/ton and at a selling price of \$46/ton, and to be competitive with ammonia from the Caribbean based on natural gas supplied at \$2/10<sup>9</sup> m<sup>8</sup> (see table 4).

3. Effect of plant location and economic advantages given for encouraging industry. The large availability of natural gas, in several developing countries and regions such as Algeria, Libya, the Middle East and the Caribbean area, coupled with the lack of large industrial outlets, has resulted in gas costs of under  $57/10^{\circ}$  m<sup>o</sup>. This gas cost can be as low as  $52/10^{\circ}$  m<sup>o</sup> in Trinidad, where this factor added with the other advantages including: good harbour facilities for shipment of products into world market, available labour, tax concessions and other official encouragements for industry, influenced W. R. Grace to expand the ammosia plant from 35,000 tons/year to 235,000 tons/year. Key to the project is also Grace's concept of marketing bulk ammonia on a world-wide basis: anhydrous liquid ammonia made by Federation Chemical Ltd. (another Grace affiliate at a 200,000 tons/ year plant at Point Lisas, Trinidad) is shipped 2,000 miles by a 9,000-ton refrigerated tanker. Ammonia cost to Carolina Nitrogen is \$10 to \$20 cheaper than on-site production would be, because of marked differences in the cost of natural gas.

Manufacturing cost and derived selling price estimated for the Trinidad ammonia plant are given in table 4. Where a comparison is made with a similar plant erected in the Middle East and based on low cost natural gas.

This comparison takes into account :

(a) For the Trinidad ammonia plant, the economic advantages mentioned above and particularly, no taxes on benefits are included;

(b) For the Middle East ammonia plant, two cases are studied:

- *Ist case.* The economics are calculated on a similar basis as for the Trinidad plant;
- 2nd case. The economics are calculated on basic data generally used for developing countries.

# II. Nitrogen fertilizers

The world's consumption of nitrogen is expected to be doubled by 1970, but increased consumption will vary widely in the different countries. In the nutritionally deficient countries, consumption is expected to be about 150 per cent more than it was in 1960. In the nutritionally sufficient countries, the growth rate will rot be as high, but these nations will account for most of the actual increase: in Europe, nitrogen consumption will increase by about 90 per cent (from 4,634,000 to 8,589,000 tons) during the decade. North America's consumption in 1970 will be about 88 per cent higher than it was in 1960.

TABLE 3. 400	MT/DAY AMMONIA	PRODUCTION BY NAPHTHA	STEAM-REFORMING (330 SD)					
Manufacturing cost and ammonia selling price								

	Unn	Unis cost (OUS)	Annual Quantity	Annual cos (10ª \$/yea)
Variable costs				
Raw materials and utilities				
Naphtha	tons	18	30.000	
Fueloil	tons	15	70,000 77, <b>500</b>	1,260
Treated water	m <sub>e</sub>	0.2	505.000	101
Catalyst and chemicals consump- tion				
Labour				158
Salaries and wages. Supervision at 25 per cent of	Men/year	5,000	100	500
salaries and wages.				125
		TOTAL VAR	IABLE COSTS	3,304
Fixed costs				
Depreciation	. At 3.5	per cent of total per cent of total per cent of total per cent of total per cent of total	investment investment investment	
		Тот	AL PEXED CONTS	3,700
elling price		MANUFA	CTURING CORT	7,004
Not cash flow at 20 per cent of total	immeterent			
Depresation provides			• • • • • •	3,220
	• • • • · · ·		• • • • • •	2,010 1,210
Not income before terms at the			• • • • • • •	2.420
The months sector that at 26 bet of				
Not income before taxes at 50 per ce Manufacturing cost	• • • • • • •		• • • • • •	7,004
Ammonia sales . Ammonia sales .	•••••		•••••••	7,004 9,424

TABLE 4. 200,000 MT/YEAR AMMONIA PRODUCTION BY NATURAL GAS STEAM-REPORMENCE

		Plant	orectes in	
<b>-</b>	Trin	ulad	Middl	e East
Investment * (\$ million)	23.5		<b>28</b> .0 °	
Variable charges d			1,500 10 ° \$	
Fixed charges •			7,150 10 * \$	
Manufacturing cost	6,900 10 ° \$		8,650 10 ° \$	
Manufacturing price		\$34.5/ton		\$43.2/ton
Selling price			Case 14	Case 21
Net cash flow at 20 per cent <sup>†</sup> of total investment.	4,700			
Net cash flow at 20 per cent # of equity	· • • •		1,850	1,850
Depreciation provides	2,940		1,150	1,150 700
Net income before taxes at 50 per cent	1,760 h		700 h	1,400 1
Manufacturing cost	6,900		8,650	8,650
Ammonia sales	8,660		9,350	10,050
Ammonia selling price		\$43.3/ton	\$46.7/ton	\$50/ton

· Including process units, off-sites and start-up expenses.

<sup>b</sup> Quoted as a non-financed plant, taking only into account additional investment owing to distance from suppliers of materials and equipment and shortage of skilled labour.

· Quoted as a financed plant.

\* Based on natural gas priced at \$2/10<sup>s</sup> m<sup>s</sup>.

\* Based on depreciation at 12.5 per cent, interest at 3.5 per cent, maintenance at 4 per cent, general plant overhead at 2 per cent, taxes and insurance at 1 per cent.

\* Return required for a five-year payout on total investment.

\* Return required for a five-year payout on equity capital only.

\* No taxes on benefits are included.

<sup>1</sup> Including taxes on benefits.

A. BREAK-DOWN OF WORLD NITROGEN FERTILIZER PRODUCTION AND GEOGRAPHIC DISTRIBUTION

An approximate break-down of nitrogen fertilizer production by products in terms of nitrogen shows that the largest category is ammonium nitrate and limed ammonium nitrate. These together account for more than one-third of total world production. Ammonium sulfate and ammonium sulfate nitrate together account for just under 30 per cent of world production. Urea, the fastest growing derivative, still represents a relatively minor portion of world production of about 8 per cent of total world nitrogen.

The distribution of nitrogen production is very much concentrated in the more industrialized countries. Some 38 per cent of it is in western Europe with another 14 per cent estimated to be in eastern Europe. North and Central America have about 33 per cent and Asia (principally Japan) about 13 per cent. These areas account for about 96 per cent of world production. However, this concentration is shifting away from these areas towards the largely agrarian developing countries with low levels of industrialization.

### **B.** TRENDS IN MATERIALS

Ammonium sulfate is expected to be used at about the same level as in the 1950s. The major increase in con-

sumption will be in other forms. Ammonium nitrate will continue to make a healthy growth, but the big growth will be in urea, ammonium phosphate and anhydrous ammonia, and also in nitrogen solutions for direct application.

### C. CHOICE OF NITROGEN FERTILIZERS

The choice of nitrogen derivatives to be produced will be determined by a number of factors. The rapid rise in production and use of urea will continue, as substantial economics in production, transportation and handling can be achieved with this highly concentrated material. On the other hand, the difficulty in using concentrated materials in areas with little experience in fertilizers may continue the preference for the more conventional forms, such as ammonium sulfate and animonium nitrate.

D. LOCATION OF NEW NITROGEN FERTILIZERS PLANT

Two factors emerge as being of critical importance in determining the course of fertilizer production:

- 1. The need for minimizing the cost of fertilizer to the farmer.
- The desire of self-sufficiency on the part of many developing countries which now import these fertilizer requirements, but which are planning for

local plants to be erected in order to shorten foreign exchange.

Several production trends are moving in this direction:

1. Plants are becoming larger.

- 2. More concentrated materials are being produced.
- 3. More use is being made of primary sources such as anhydrous ammonia.

With regard to the plant location, several concepts of fertilizer supply can be envisaged:

- 1. Fertilizer production close to raw material sources and import of finished products to consuming countries.
- 2. Production at the sources of raw materials confined to primary products, such as anhydrous ammonia with finished products manufactured by the consuming countries.
- 3. All production concentrated in the consuming countries using imported raw material.

Imported finished fertilizers have been for many of the developing nations the principal source of nutrient materials. Increasingly, however, local plants have been erected to supplant these imports. But recently, increasing interest has been shown in the shipment of intermediate compounds such as ammonia. Such a concept may be an effective compromise that would at least partially satisfy the developing countries' desires for their own production of fertilizers and the shortage of foreign currency, and at the same time significant economics would be achieved by transforming the more concentrated intermediate materials produced in larger plants.

However, there is not a general and ideal solution to this problem. Such matters as: foreign exchange problems; availability or non-availability of raw materials as natural gas and naphtha at low prices, and of auxiliary raw materials as sulfur or phosphate rocks; geographic location; possibilities of barter agreement contracts, will all play a part in determining which would be the best under the particular circumstances involved.

Such a comparison between the different possibilities concerning the extent of the manufacture of fertilizers and the location of the plant, could be made, taking into account: the economic data presented in section E below, the freight rates which can be based on known charterings or, when no recent information is available on bookings for other commodities moving on similar routes.

# E. DESCRIPTION AND ECONOMICS OF NITROGEN FERTILIZERS MANUFACTURE

Description and economic data are given hereunder for the following productions: sulfuric acid, nitric acid, animonium nitrate, animonium sulfate, and urea.

# 1. Sulfuric acid

The production of sulfuric acid based on petrochemical sulfur is not generally carried out close to the gas fields. For reasons of economy, sulfur produced on the field is

# transported and acid is manufactured in the consumption areas.

There are two industrial manufacturing processes which are, the chamber process and the contact process. For many years the chamber process was the only method used. But now the contact process, which is more flexible and produces a more concentrated acid, has become more popular.

# Economics of sulfuric acid manufacture

The elements of the operating cost for a 70,000 tons/ year plant based on sulfur feed-stock are given below:

Investment				
Process units (\$ million)				1.3
Raw material consumption				
Sulfur (tons/year)				°3,500
Utilities requirements				
Electricity (10 <sup>a</sup> kWh/year)				700
Cooling water (10 <sup>e</sup> m <sup>2</sup> /year)				1,800
Process water (10 <sup>s</sup> m <sup>3</sup> /year)	• •		•	55
Steam produced (10 <sup>a</sup> lons/year).	• •		•	45
Labour				
Men/shift	•	•		7
Men/day	•	•	•	2

# 2. Nitric acid

Prior to the end of the Second World War, nitric acid was mainly used for the manufacture of explosives: nitroglycerine, trinitrotoluene, cellulose nitrate and ammonium nitrate. The production was considerably increased during war time.

At the end of the war, the market of nitric acid was considerably changed by the growth of the fertilizer industry and the use of ammonium nitrate as fertilizer. Now the greater part of all nitric acid produced is used for the production of agricultural fertilizers; this acid is required in a dilute form (50-60 per cent). A stronger acid (95 per cent) is needed to produce organic nitrates and nitro compounds, used in the explosives and dyestuffs industries.

# (a) Manufacturing processes

Commercial manufacturing processes of nitric acid are based on the following steps: direct air oxidation of ammonia and NO<sub>2</sub> absorption by water

$$4 \text{ NH}_3 + 5 \text{ O}_3 \rightarrow 4 \text{ NO} + 6 \text{ H}_3\text{O} \tag{1}$$

$$\frac{2 \text{ NO} + \text{O}_1}{1 \text{ NO} + \text{H}_0} \rightarrow \frac{2 \text{ NO}_2}{1 \text{ NO}_2}$$
(2)

$$NO_1 + H_2O \rightarrow 2 NO_3H + NO$$
 (3)

Processes differ in the operating pressures of oxidation and absorption:

Licensers	Processes of emblation	Presence of above, plan
C and I Chemico	High	High
Grande Paroise	Medium	High
Montocatini.	Medium	Medium
Kuhimann Stamicarboa	Low	Madinus

### (b) Economics of nitric acid manufacture

The elements of the operating cost for a 60,000 tons/ year plant are given below:

Investments Process units (\$ million)	1.25
Process units (3 minion) = .	1.43
Raw material consumption	
Ammonia (tons/year)	16,200
Utilities requirements	
Electricity (10 <sup>8</sup> kWh/year)	600
Cooling water (10 <sup>a</sup> m <sup>a</sup> /year).	9,000
Steam produced (10 <sup>a</sup> tons/year)	7.5
Chemicals and catalyst consumption	
Platinum: .kg/year)	12
Labour	
<b>Men</b> /shift	6
Men/day.	1

### 3. Ammonium nitrate

Until the end of the Second World War, the principal customer of ammonium nitrate was the explosives industry. It was not much used as fertilizer b-cause of its hygroscopic tendency; indeed, instead of remaining in a granular form, it set in large blocks. By making the crystal size uniform and coating the crystals with clay or kieselguhr, this problem was solved.

Now, ammonium nitrate granules are currently used as fertilizers. Typical solutions of ammonium nitrates contain 34.5, 33.5, 27.5 and 20.5 per cent of nitrogen, the most concentrated fertilizers remaining superior today. Ammonium nitrate is either consumed as such, or mixed with ammonia or ammonium sulfate.

### (a) Manufacturing processes

Ammonium nitrate processes are based on nitric acid reutralization by ammonia. The most important are given below:

### (i) Frilling process

Nitric acid reacts with ammonia vapour in an agitated vessel made of stainless steel. The solution concentrated to 85 per cent by the heat of reaction. Then, by evaporation under vacuum the concentration is increased to about 95 per cent. The solution is pumped to the top of a tower and is dropped through a spray head. Air is blown countercurrently and nitrate solidifies in little pellets: the "prills". The prills are filtered, dried, and then mixed with clay or carbonate.

### (ii) Vacuum crystallization process

A solution containing about 60 per cent of nitrate is obtained in a reactor. This solution is concentrated by evaporation and sent to a vacuum crystallizer, giving accurately fixed size of crystals. These crystals are separated by centrifugation, dried and mixed with clay, kieselguhr or carbonate.

### (iii) Stengel process

In a packed reactor, ammonia vapour is mixed with a 60 per cent nitric acid solution. Water is eliminated by the heat of reaction in a separator. Ammonium nitrate is obtained in a molten state. It is solidified by cooling and then ground; the granules are conditioned with clay.

# (b) Economics of ammonium nitrate manufacture

The elements of the operating cost for a 75,000 tons/ year ammonium nitrate production are given below:

Investments										
Process units (\$ million)	·					•	•	•		1.4
Raw materials consumption										
Ammonia (tons/year)										16,800
Nitric acid (Ions/year).	 •	•	•	•	•	•	•	•	•	<b>63,00</b> 0
Utilities requirements										
Electricity (10 <sup>s</sup> kWh/year)										1,400
Stean: (10 <sup>s</sup> tons/year)										165
Cooling water (10 <sup>a</sup> m <sup>a</sup> /year)	 •	•		•	•	•	•		•	<b>57</b> 0
Labour										
Men/shift										4

### 4. Ammonium sulfate

1

Ten years ago all the ammonium sulfate was produced in by-product coking plant, by the reaction of ammonia in the coal gas with sulfuric acid. At present, owing to the increase of ammonia units, ammonium sulfate is made by direct neutralization of sulfuric acid by synthetic ammonia.

Ammonium sulfate is often used as fertilizer, mixed with ammonium nitrate.

### (a) Manufacturing processes

Man/day . .

Manufacturing processes of ammonium sulfate differ only in minor details.

Ammonia and sulfuric acid react directly; ammonium sulfate is crystallized, separated by centrifugation and then dried.

### (b) Economics of ammonium sulfate manufacture

The elements of the operating cost for a 100,000 tons/ year ammonium sulfate plant are given below:

### Investments

Process units (5 million) .		•	 	•	 0.45
Raw materials consumption					
Ammonia (tons/year) Sulfuric acid 98 per cent (tone					
Utilities requirements					
Electricity (10 <sup>2</sup> kWh/year)	· .		 		 1.700
Fuel gar (10 <sup>e</sup> m <sup>s</sup> /year)					190
Stearn (10 <sup>s</sup> tons/yes.r)					18
Cooling water (10 <sup>e</sup> m <sup>8</sup> /year).					120
Labour					
Men/shift			 		 2
Maniday					 1

# 5. Urea

Urea has the highest nitrogen content (46 per cent) among the solid fertilizers. Its main characteristics are: a high solubility, easy handling and storage and nonexplosive properties.

Improvements in processes, lower costs of materials and erection of larger capacity units have cut down the urea process, from \$142/ton in 1952 to \$81.25/ton in 1962.

The greater part of urea is used as fertilizer; it is also employed as animal feed.

# (a) Manufacturing processes

The manufacture of urea is carried out in two steps: First step — ammonia and CO<sub>2</sub> react under pressure, giving ammonium carbamate

$$2 \text{ NH}_3 + CO_3 \rightarrow \text{NH}_2\text{COONH}_4$$

Second step — carbamate is decomposed into urea and water

$$\text{NH}_1\text{COONH}_4 \rightarrow \text{NH}_1\text{ CUNH}_3 + \text{H}_2\text{O}$$

This dehydratation is not a total reaction; a part of carbamate remains unconverted; it is separated from the mixture by decomposing it to gaseous  $CO_2$  and ammonia.

There are several ways of using the mixture ammonia- $CO_8$  obtained by the decomposition of the carbamate: either send all ammonia in an adjacent fertilizer unit, or recycle all or a part of the mixture. Urea solution is then concentrated under vacuum, and sent to a granulation tower.

All the commercial processes differ only in operating conditions, the ratio ammonia- $CO_1$  in the feed, and the manner of handling the  $NH_3$ - $CO_2$  mixture.

The principal urea processes are the following: Chemico, Du Pont, Inventa, Montecatini, Péchiney, Stamicarbon, Toyo Rayon.

# (b) Economics of urea manufacture

The elements of the operating cost for a 120,000 tons/ year plant are given below:

Investments	
Process units (\$ million)	4.7
Raw materials consumption	
Ammonia (tons/year)	1,000 # 500
Utilities requirements	0,500
	0,000
Steam (10 <sup>8</sup> tons/year)	66/)
Cooling water (100 m8/waar)	1.300
Labour	1,500
Men/shift	13
	2

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# 2. AMMONIA MANUFACTURE FROM PETROLEUM FEED-STOCKS

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It has long been recognized that the addition of various chemical fertilizers, containing appropriate forms of nitrogen, phosphorus, and potassium, can substantially increase the yield and quality of almost all agricultural crops. The volume use of chemical vertilizers containing these three primary plant nutrients was well established in many countries by the turn of the century, and has continued to grow to the present time. In the last two or three years, the importance of fertilizers to agricultural economies throughout the world has been a subject of particular attention both in industrial and governmental circles. Government planners are becoming particularly aware of the important potential which fertilizers represent to achieve the ever-growing agricultural outputs that will be necessary for expanding populations. Industry, on the other hand, has shown increasing interest in participating in this increasingly important segment of the chemical industry, as fertilizers represent a large volume product with excellent growth prospects.

The manufacture of nitrogen fertilizers has been of particular interest, as the demand for these products has grown faster than for phosphate or potassium fertilizers. The higher growth rates for nitrogen fertilizers are due in part to the fact that the volume production or these materials has developed more recently than for phosphate and potash fertilizers, and in part to the fact that the crop responses to nitrogen fertilizers are inore directly apparent.

Nitrogen fertilizers today are almost without electron produced from ammonia, principally synthetic, but including significant by-product ammonia. The principal nitrogen fertilizer materials include ammonia sulfate, ammonium nitrate, urea, and such multi-nutrient materials as ammonium phosphate and nitrophosphates. Since it is the nitrogen content of these materials which is of prime importance, they are commonly compared on a basis of their equivalent nitrogen content; ammonium sulfate contains 21 per cent nitrogen, pure ammonium nitrate 33.5 per cent nitrogen, and urea, 45 per cent nitrogen. Anhydrous ammonia itself contains 82 per cent nitrogen, and is an increasingly popular fertilizer material for application directly to the soil, primarily in the more developed countries where the necessary heavy investment in application equipment is possible.

It is important to examine the economic incentive for the use of fertilizers, for the fact that the application of fertilizers increases the crop yields is only part of the story. The use of fertilizer is an economic advantage to the farmer only if the total cost of applied fertilizers is significantly less than the value of the increased crop outputs. While absolute increases in crop yields may be important from a governmental planning standpoint, the use of fertilizers is hardly attractive for farmers if \$40 spent on fertilizers returns only \$40 in value of increased crops. Therefore, it is of particularly critical importance in considering the use of fertilizers to keep in mind at all times the ratio between crop prices and fertilizer prices. It goes without saying in this context that the advantages of fertilizer use are adversely proportional to their cost to the farmer, and every effort must be made to keep the price which the farmer must pay to an absolute minimum.

The total consumption of nitrogen fertilizers in the world is estimated at over 12 million tons of nitrogen equivalent in 1962-1963. This is equivalent to 15 million tons of ammonia. Adding to this the requirements for industrial uses, the total demand for ammonia was approximately 18 million tons in 1962-1963.

The first use of chemical nitrogen fertilizers dates back to the early exploitation of the natural sodium nitrate deposits in Chile during the middle of the nineteenth century. For many years, these were the prime sources of nitrogen fertilizers throughout the world, and production reached a maximum annual output of approximately one and one-half million tons.

Prior to the First World War, Fritz Haber developed a process for producing ammonia catalytically from a mixture of nitrog n and hydrogen. The first commercial plant using this process was built in Germany in 1910, and soon thereafter a number of plants were built using this process. Although sodium nitrate production from Chile has continued, the growth of materials based on synthetic ammonia has been so great that today Chilean nitrate represents less than 1 per cent of the total world fertilizer nitrogen supply.

The growth in consumption of fertilizer nitrogen throughout the world is shown in figure I.

As might be expected, this consumption has been concentrated in the areas of the world with the most highly developed agriculture, namely in Japan, Europe, and North America. These three developed areas together represent over 80 per cent of the total world consumption. The individual countries with the greatest consumption of nitrogen fertilizers are presented in table 1.

WORLD TOTAL		10,504
Total		3,215
Other North and South America	337	
Mexico	128	
United States	2,750	
North and South America		2,019
TOTAL		
Other Asia and Oceania	393	
China (Taiwan)	107	
South Korea	219 200	
China (mainland).	440	
Japan	660	
Asia and Oceania		
TOTAL	•	
Other Africa	154	
United Arab Republic	190	
Africa		4,920
Τοται		-
Other European	102 862	
Sweden	106	
Denmark	124	
Czechoslovakia.	145	
Eastern Germany.	245	
Spain	274 270	
Italy	351	
United Kingdom.	460	
France	600	
Foderal Rep. of Germany	618	
USSR	769	

 TABLE 1. WORLD CONSUMPTION OF NITROGEN FERTILIZERS, 1961

 (Thousands of metric tons nitrogen)

The countries that are most developed agriculturally are at the same time the most industrialized countries, and we are not surprised to find that the production of nitrogen fertilizers is concentrated largely in the same countries. Moreover, the amount of production in these industrialized areas is more than sufficient for their own requirements, and the trade patterns show that these countries do in fact provide a substantial portion of nitrogen fertilizers for the developing countries, as shown in table 2. This situation is changing rapidly, and will be a principal point of discussion in the present paper. Increasing dissemination of improved technology in the manufacture of ammonia and its derivative products, together with active industrialization programmes in most of the developing countries, are stimulating the domestic manufacture of nitrogen fertilizers in the developing countries where consumption levels, while relatively low, are expected to grow rapidly in the future.

The manufacture of the various nitrogen fertilizer materials from synthetic ammonia, while requiring

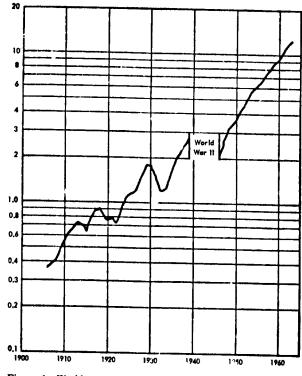


Figure 1. World consumption of nitrogen fertilizers (millions of metric tons of nitrogen)

substantial capital investments, is not complex. Ammonia is reacted with sulfuric acid, or alternatively with gypsum, to produce ammonium sulfate. Ammonia is combined with nitric acid, itself produced from ammonia, to produce ammonium nitrate, and this product can be diluted with varying quantities of limestone to produce limed ammonium nitrate materials to reduce explosive hazards. Ammonia is reacted with carbon dioxide to produce urea. Chemical compounds containing both nitrogen and phosphorus can be produced in the form of ammonium phosphates by reacting ammonia with phosphoric acid, and in the nitrophosphates by reacting phosphate rock with nitric acid.

 TABLE 2. PRODUCTION AND CONSUMPTION OF NITROGEN MATERIAL, 1961

 (Thousands of metric tons of nitrogen)

	Production	Consumption	Production excess
Europe	6. <b>876</b>	5,766	+ 1,110
Africa	127	389	- 262
Asia	1.763	2.089	- 326
Οσαπία	20	35	- 15
North and Central America	4.438	4.136	+ 302
South America	207	187	+ 20
	13,431	12,602	

By far, the largest capital investment requirements are tied up in the ammonia plants. The manufacture of these various derivatives is usually the minor part of an overall nitrogen fertilizer complex. Therefore, it is appropriate to focus attention on the various factors involved in the manufacture of anhydrous ammonia as the prime building block on which a nitrogen fertilizer industry must be based.

As mentioned previously, synthetic ammonia is produced by catalytically reacting a highly purified mixture of three volumes of nitrogen with one volume of hydrogen. Elevated temperatures and pressures are necessary for this reaction to take place. Even the most effective catalysts do not achieve significant rates of reaction below about 300°C, and most operations are generally carried out between 400 and 600°C. Increasing pressures are also highly effective in promoting the reaction. There is a considerable variation among the several processes used for the production of ammonia, in the pressures at which they operate, ranging from 100 atmospheres to as high as 1,000 atmospheres.

There is also a wide variation in the raw materials and processes used to obtain the purified mixture of three volumes of nitrogen and one volume of hydrogen, and the choice of these raw materials and processes is one of the primary variables affecting the ultimate cost of ammonia.

The nitrogen for this mixture is almost invariably obtained, by one means or another, from atmospheric nitrogen, which comprises about 79 per cent of the air we breathe. The hydrogen can be obtained from water, from the hydrogen chemically combined in various petroleum feed-stocks, or from coke-oven gases.

Perhaps the simplest process from a chemical standpoint, although quite costly compared to others used, is the preparation of ammonia by the electrolysis of water and the liquefaction of atmospheric air. Water when electrolyzed dissociates into pure streams of hydrogen and of oxygen. Liquefaction of air produces separate streams of nitrogen and oxygen. The nitrogen obtained by the liquefaction of air, and hydrogen from the electrolysis of water can then combine with relatively little additional purification to form a suitable ammonia synthesis gas. Such plants are in operation in Iceland and in the United Arab Republic but, as mentioned previously, capital and operating costs are quite high for this process. Furthermore, it is highly desirable to find uses for the two oxygen streams to provide some by-product credit to offset the high cost of operation.

Synthesis gas can also be produced from coal, by two somewhat different methods. The older method involves the reaction of coal or coke with air and steam, to produce a mixture of carbon monoxide and dioxide, hydrogen, nitrogen, and various hydrocarbons. By various means the products other than nitrogen and hydrogen are removed, and a synthesis gas is ready for conversion to ammonia.

Alternatively, coal can be reacted with a pure oxygen stream and steam to produce a mixture of hydrogen and other gases. After purification, this hydrogen stream is reacted with a stream of pure nitrogen from an air liquefaction plant to produce the desired synthesis gas.

We turn now to the most important and commonly used processes by which the synthesis gas is produced from a variety of petroleum feed-stocks. These are the steam-reforming process and the partial oxidation process. In the reforming process hydrocarbons are allowed to react with steam over a catalyst at elevated temperatures to form hydrogen, carbon monoxide, and small amounts of carbon dioxide and water. It is generally necessary that the hydrocarbons feed-stocks be free of sulfur. The gases leave the primary reformer with up to 8 per cent methane and then go to a secondary reformer where sufficient air is admitted to supply the necessary nitrogen for the final synthesis gas. In this secondary reformer, the methane content is reduced and additional carbon monoxide and hydrogen reformed. In a shift converter, the carbon monoxide reacts with steam to form additional quantities of hydrogen and carbon dioxide, which is removed from the gases by scrubbing, generally with monoethanolamine. The small amount of unconverted carbon monoxide can be converted to inert methane by methanation.

In the partial oxidation process the hydrocarbon is introduced with preheated 95 per cent oxygen from an air separation plant into a combustion reactor, where carbon monoxide, hydrogen, water vapour and a small amount of carbon dioxide are formed. There may be as much as  $^{-3}$  per cent solid carbon in these gazes where heavy o. are the feed-stock. After its removal, the gases pass to the shift converter where the carbon monoxide reacts with steam forming hydrogen and carbon dioxide.

The use of an oxygen stream requires that an air liquefaction process be operated and the nitrogen stream from this liquefaction plant is reacted with the pure hydrogen obtained by the partial oxidation. This process is the most flexible of any of the synthesis processes and can be operated on natural gas, refinery off-gas, light hydrocarbons, heavy hydrocarbons, crude oil, or powdered coal. The steam reforming process is particularly ad aptable to natural gas, liquefied petroleum gas, and light naphtha feed-stocks.

There is another process involving low-temperature separation, which is used on gas stream containing significant quantities of hydrogen. such as coke-oven gases and reformer off-gases. In this process, the hydrogencontaining gas is scrubbed with liquid nitrogen from an air separation plant. All gases except hydrogen are condensed and sufficient nitrogen is vaporized during the scrubbing process to provide the required 3:1 ratio of nitrogen and hydrogen for a synthesis gas.

In the early days of the Haber process, the feed-stock used for almost all ammonia production was coal or coke; this situation continued up into the Second World War. It was not until the late 1940s that the first petroleum-based ammonia plants were built, when plants were constructed in the United States based on natural gas using the steam-reforming process. As new capacity was needed, additional plants were constructed, invariably using hydrocarbons as their feed-stocks, in almost all cases natural gas. In the 1950s, the partial oxidation process was developed to the point of commercial utility and several plants were built in the United States, in Peru, in Europe, using fuel oil or crude oil, as the basic material feed-stock.

The development f catalytic reforming in petroleum refining industry produced significant by-product hydrogen streams which themselves became feed-stocks for a number of ammonia plants. However, further developments in petrolcum refining, particularly the hydrogentreating process, produced requirements for this byproduct hydrogen within the refineries themselves, and few further plants were built based on refinery hydrogen.

Regardless of the petroleum feed-stock uses, it soon became apparent that substantial economies in the manufacture of ammonia were possible using hydrocarbon feed-stocks rather than coal based processes and a significant shift in this direction has been taking place throughout the world. Japan, in particular, finding itself at a competitive disadvantage in important export markets, has effected a rapid shift from coal 10 petroleum based ammonia processes.

Table 3 shows the approximate break-down of the feed-stock material used in recent years for the production of ammonia in various sections of the world. The predominance of petroleum hydrocarbon feed-stocks is clearly apparent here.

Plants are still being built using coal or lignite sources, or based on the electrolysis of water. Furthermore, recent interest has developed in the United States in the low temperature separation of hydrogen from coke-oven gas stream on the part of the large steel companies, and this raw material source will continue to be exploited. However, the shift towards petroleum feed-stock sources is anticipated to continue.

The particular hydrocarbon feed-stock that will be chosen as a basis for an ammonia plant will be determined largely by the relative price of each of the various feedstocks available in the area in which production is planned and to a lesser extent by the process limitations imposed by the feed-stock selected. As pointed out in a previous section, the petroleum feed-stocks that can be used for the manufacture of ammonia range from various gaseous hydrocarbons to heavy fuer oil and crude oil.

The refining of crude oil produces a variety of separation fractions including asphalt, tar, and residual fuer oil at

TABLE 3. DISTRIBUTION OF RAW MATERIALS FOR SYNTHETIC AMMONIA MANUFACTURE, 1961 (Percentage of total ammonia production)

4 <del>11</del>	Priroloum based	Coni	<b>Electroly</b> tic	Other
Western Europe	41	51	6	2
United States	95	1	Ă	
Japan	56	33	10	1
Other countries *	63	27	10	_
TOTAL DISTRIBUTION 8	57	36	6	1

\* Excluding countries with centrally planned economies, for which information is incomplete.

the heavy end through to gas, oil keroscne, naphtha (or gasoline), and various gaseous hydrocarbons, such as propane, butane, and methane. The relative amount of each of these fractions depends on the particular crude oil and refinery process equipment. The ultimate proportion of the various fractions produced would under ideal circumstances closely match the natural demand for these products. However, the demand both on a world basis and in many individual, consuming countries is substantially out of balance with the relative proportion of the various petroleum fractions which can be obtained by normal refinery processes.

At the present time, the 'ight hydrocarbons which consist of natural gas, the LP gases (propane and butane), and naphtha are in world-wide over-supply. Large volumes of natural gas (and its contained LPG) are being flared or reinjected into oil fields, and there are substantial reserves of natural gas which remain undeveloped due to insufficient markets. Similarly, the naphtha and in some countries the LPG produced in refining operations are currently in over-supply and there is considerable pressure to find outlets for their use.

A basic reason for the naphtha surplus has been more rapid expansion in the demand for the fuel oil and middle distillates compared to gasoline. The rapid growth of the fornier has been accelerated by their being substituted for coal in many uses. The lighter ends, on the other hand, principally gasoline, are dependent or the growth of transportation. Rather than displacing other fuels, gasoline has itself been displaced by middle distillates in motor fuels and kerosine based jet fuels in aviation fuels. A further aggravating factor in the development of the chronic naphtha surplus situation has been the increasing availability of the lighter high naphtha bearing crudes.

The result of this surplus of the lighter hydrocarbons. both gaseous and in the naphtha range, has brought about a decline in values approaching fuel value in many markets. This surplus is expected to persist for some time. For this reason, naphtha is increasingly being considered as a primary feed-stock for ammonia manufacture, and we expect that many of the additional plants to be built will use naphtha.

Within local market areas the prices attached to various petroleum fractions are not entirely a matter of natural supply demand but often are substantially altered by government policies. Government restrictions on naphtha imports either through quotas, duties, or the imposition of taxes for specific purposes or the establishment of fixed price levels, can create an artificial price situation. Under these circumstances local prices may not bear logical relation to world prices.

The prices or values of local natural gas are even more subject to government policy than for naphtha. Where gas reserves are exploited, particularly when they are limited, premium fuel uses are emphasized and the gas is priced accordingly. When available, natural gas is generally the preferred raw material for ammonia, due to lower investment and operating costs. However, in the absence of local natural gas, naphtha will generally be the preferred economic feed-stock particularly in view of the depressed pricing situation previously referred to.

### TABLE 4. COST OF AMMONIA MANUFACTURE

Raw material: Capacity: 400 Flxed investm	T/SD, 140,000 T/yr.	0	
Auxiliaries			
	300,00	0	
· · · · · · · · ·	Ownitties	8/south	1/ma NH,
Variable costs			
Natural gas	31.0 MM BTU	0.49	12.49
Power		0.009	6.30
Cuoling water		0.015	0.94
Boiler water feed		0.90	0.27 1.10
			21.01
Semi-variable costs			
Operating labour		2.80/hr	0.87
Supervision		8,000/yr	0.23
Maintenance	1 superintendent	13 <b>,000/ yr</b>	0.09
	3-1/2 per cent of investment/yr 30 per cent of operating labour and		1.82
	supervision		0.36
			3.37
Fixed costs excluding capital charges			
Plant overhead	70 per cent of operating labour and supervision		6.83
Depreciation	6-2/3 per cent of investment per year		3.40
Local taxes and insurance	1-1/2 per cent of investment per year		0.78
			5.00
	TOTAL COPT OF MANUFACTURE	L	<b>\$29.4</b> 7

In summary, we have seen the rapid displacement of coal with petroleum-hased feed-stocks as the preferred feed-stock for ammonia. This initially was in the form of plants based on natural gas; more recently, proceeses using the various liquid feed-stock materials have been introduced. The future will continue to find petroleum feed-stocks displacing coal; we expect that many ammonia plants in the future will be based on naphtha, which will be in chronic surplus and will be priced close to fuel value in most areas.

While naphtha will probably be a major source of new ammonia plants in many areas, the availability of lowcost natural gas in petroleum-producing areas, such as Kuwait and Libya, many lead to the construction of large ammonia plants at these points. Natural gas is difficult and costly to transport, and therefore tends to be a local energy source. The recent development of feasible means of bulk shipment of refrigerated anhydrous armmonia now makes it possible to consider production in large low-cost plants at these sources of cheap astural gas, with subsequent shipments to consuming meriate. This will be discussed in some detail at a later point in this paper.

Turning now to the cost of manufasturing ammonia, we present in table 4 a typical cost break-down for the manufacture of ammonia, from which the effect of the several important variables can be calculated. The cost break-down we have shown is for a plant making 400 short tons of ammonia per day or 140,000 tons per year. These investment costs are shown for a location on the United States Gulf Coast, and the plant is based on the high-pressure reforming of natural gas.

The unit consumption of natural gas, power, and water shown here are typical, but these may vary substantially depending upon the specific plant design. This particular estimate is based on the use of electric-meter drives for the compressors. By substituting gas engines for these electric motors, the gas requirements would be increased by about 10 million BTUs per ton, and the total power consumption reduced to approximately 100 kWh per ton. At the same time, however, the investment costs and maintenance charges would also be increased to take care of the added expense involved in maintaining the gas-engine drives. It is also possible to reduce the substantial water requirements shown by using aircooled heat exchangers, but this would increase the investment required for the plant.

The auxiliary facilities required would have considerable influence on the total investment and on the cost of manulacture. The estimate shown here is based on a grass roots plant. Of the \$7.3 million total investment shown, only \$5.8 million is actually for the ammonia processing facilities with the difference being required for auxiliary facilities such as site improvements, power substations, buildings, cooling towers etc. Storage costs are often substantial. In this particular estimate, storage has been provided for 15,000 tons of anhydrous ammonia at a cost of \$890,000.

On this basis and with the assumption: used, the manufacturing cost of ammonia in this particular plant comes to \$29.47 per short ton of ammonia. This manufacturing cost figure is of course only far the precise conditions outlined in this table. If any of several parameters are changed, the cost of manufacture will change, and it will be of particular interest to examine exactly how changes in these factors will affect the change of manufacturing cost.

The primary factors, whose change can materially affect the cost of manufacture and which we will examine here, will include the following

- (a) The size of plant;
- (b) The raw material used.
- (c) Electric power costs;
- (d) The area in which the plant is constructed.
- (e) The cost and size of the labour force.

Let us consider first the size of the plant. In most chemical processes, the cost of plant investment increases more slowly than the capacity of the plant. If plant A has twice the capacity of plant B, the cost of investment of plant A will be substantially less than twice the cost of plant B. In other words, the investment cost per ton of output is less for plant A than for plant B. Thus, those charges which are proportional to plant Investment, such as depreciation, insurance, and taxes, will be lower per ton of output in the case of plant A than in plant B. Furthermore, a lower profit margin will be necessary per ton of output from plant A than from plant B, to give an equal return on investment. It is possible to express the relationship of investment costs to plant capacities with increasing size its putting the increases in investment cost in terms of the capacity increases, raised to a power less than 1. An analysis of the detailed eligineering costs for various size high pressure reforming plants based on natural gas one example of which was cited in the previous table, shows that the investment costs go up by the capacity ratio raised to the  $^{-1}$  power. Thus, if the plant size is doubled, the investment cost in this particular case increases by a factor of  $^{-2}$ . For 1.66

Esing this relationship we can calculate the effoct of varying size for this particular type of plant and have presented figures for plant size: raiging from 200 tons per day to 1 000 tons per day in table 5. This table shows that a 200 ton-a-day plant would have an investment charge of \$64.29 per annual ton of capacity whereas a 1,000 ton-per-day plant would have a much lover investment charge of \$49 per annual ton of ammonia.

As can be seen from the previous cost break-down presented, several important factors are related to the size of the investment. In this break down maintenance charges plant depreciation lineal taxes, and insurance are roughly proportional to the total investment per ton of product. Therefore, all of these charges will be in the case of the 1,000 ton-per-day plant roughly two-thirds of the cost for a 200 ton-per-day plant. Furthermore, there will be substantial economies in the labour and supervision costs in the larger plants, as this work force is a relatively constant factor and does not increase proportionally to the output of the plant.

The not effect of variations in plant size on the direct manufacturing cost of ammonia, neglecting for the moment profit margin is shown in figure 11. Here we see the manufacturing cost varies from \$33.25 per ton in the case of a 200-ton-a-day plant to \$26.63 per ton in the case of the 1,660-ton-per-day plant.

As noted above there would also be a substantially reduced profit margin necessary in the one of the larger nlant to return an equivalent return on investment. For example, to return 20 per anni before taxes in the one of the 200 ton-per-day plant, would require 20 per cent of the 564.29 investment charge per annual ton, or \$12.86 per ton of ammonia. In the case of the 1.600-tonper-day plant, a margin of only \$5.60 would return the same 20 per cent.

TABLE S. CAPITAL INVESTIGATION FOR ANDIDANA FOR VARIANTS SUB PLANTS Inno: High-pressure referming of natural gas under Gulf Coast conditions

Short tons per day		-			1.00
Short tens per year	16,000	144,500	214,000		359,689
Battory limits areatsaget (\$ rollion)	3.6	5.8	77	9.5	11.2
Austiliary facilities (5 million)	8.9	1.5	1. <b>9</b>	2.4	2.0
Tetal (6 million) a construction of a construction	4.5	7.3	9.6	H.9	14.0
Dullan per contra cas.	64.39	<b>31.10</b>	41.70	4.4	49.48

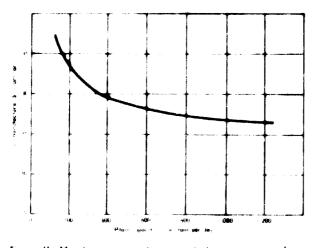


Figure 11 Manufacturing cost for ammonia for various size plants Process high pressure reforming of natural gas

Busts

Investment Cost Coust conditions Natural gas 40 # million BTU Pewer 9 milliok Wh

The effect of the raw material on cost relates principally to the cost of the raw material, although some variation in investment costs and investment-associated costs will result, depending on the material chosen. Cost variations due to varying raw material costs can be illustrated by examining the range of prices of natural gas throughout the world. These may run from 5 ¢ per million BTUs in petroleum producing countries, to 60 ¢ per million BTUs in loss favoured areas. On the basis of a requirement of 31 million BTUs per ton of ammonia, raw material costs would run from \$1.55 per ton of ammonia, for 5 ¢ gas, to \$18.60 per ton of ammonia, for 60 ¢ gas. Thus, there would be a difference of \$17.05 between the two eases cited.

It should be noted that such a wide range in cost as ested for natural gas would not generally be expected for materials such as neglethe. Natural gas being difficult and eastly to transport would be valued in accord with the domand at the point of production, whereas materials such as neglethe, which are relatively easy to transport, would tend to have a nervower range of costs since they can be easily transported from the point of production to points of domand.

The second manufacturing cost variable associated with rew materials is related to the substantial differences in process-plant investment for processes using the difference raw materials. In the example oited, the high-processor reforming plant based on natural gas and having a appointy of 60 tens per day would show a total investment of \$7.3 million. A plant of similar size based on high-processor reforming of naphtha would have a cost of \$0.1 million, and operating costs as shown in table 6. A plant based on the low-temperature expandion of reformer off-gas would cost \$6.8 million, while a costbased plant using steam-oxygen gasification would require \$10.5 million. These differences in cost due to the variations in investment have in general a lesser effect than variations that might be found in the cost of raw materials. For example, as shown in table 6, a plant based on naphtha would have a manufacturing cost of some \$3 per ton higher than one based on natural gas, assuming both raw materials had equivalent prices on a BTU basis. One dollar and sixty cents of this difference would be accounted for by the greater BTU requirement for a naphtha based plant compared with a natural gas plant.

Electric power costs are quite significant for the manufacture of ammonia; in the case of the cost breakdown presented for the natural gas plant, these amounted to 36.30 per ton of ammonia on the basis of 9 mill power. Obviously, higher power rates would substantially increase the cost, each additional mill in the cost of power amounting to 70 ¢ per ton of ammonia. If natural gas prices are sufficiently low, it may be preferable to consider gas-engine drive for compression units. Although the investment cost would be somewhat higher, in this case the savings possible through low natural-gas costs would more than offset this.

In considering the development of the petrochemical industry in the developing countries, it is important to examine the differences in cost which would arise from the fact that the plant is being constructed and operated in an industrial atmosphere quite different from that found in the more developed countries. These differences arise for many reasons, including the general lack of skilled labour both for construction and operating purposes, the lack of adequate supervisory talent, the existence of government regulations imposing heavy burdens of licensing and controls, problems associated with the limited availability of foreign exchange, and extended delays in plant construction.

It has been our experience in examining a number of lasts in developing countries, that investment required for a plant in such an area is at least 20 per cent his ter. than a similar plant built in an industrialized country; in many cases, this differential may be well in excess of 30 per cent. This is brought about by several principal factors. In the first place, the lack of foreign exchange leads to a number of difficulties in construction an operation which substantially add to the plant cost. It may be necessary to purchase component parts of the ant, such as motors, from high cost local production plants rather than importing them from lower cost sources abroad. It may be necessary to use local construction firms, which although having lower labour costs will generally because of inexperience and unfamiliarity with the method of construction be more costly to use than bringing in construction crows from abroad. There may be substantial costs associated with training local labour in the toshniques required for plant construction, maintenance, and operation.

Another factor of some importance is the longer period of time generally necessary for construction of plants. It has been our experience that this is very often at least twice as long as the time necessary for construction in a more industrialized area. For example, a plant that could be created in twelve months in Europe, might easily require twenty-four months in a relatively unindus-

# TABLE 6. COLT OF AMMONIA MANUFACTURE

Process: High pressure reforming Row material: Naphtha	
Capacity: 400 T/SD, 140,000 T/yr	
Fixed investment:	<b>₿US</b>
Process plani	6,600,000 1, <b>50</b> 0,000
	8,100,000

	Quantities	S-unis	\$.short to of NH <sub>k</sub>
Variable costs			
Naphtha	35.0 MM RTH (1.706 (be)	0.40	
rower	7.5 kWh	0.40	14.00
Cooling water	70 M	0.009	6.43
Botter feed water	0.4 M mil	0.015	1.05
Catalyst, chemicals, supplies		0.90	0.36
			1.50
Semi-variable costs			23.34
Operating labour	5 mm/shift		
Supervision	A foremen	2.80/hr	0.87
	l surcrintendent	8,000/yr	0.23
Maintenance	3-1/2 mer cent of instruction	13 <b>,00</b> 0/yr	0.09
Labour overhead	30 per cent of operating labour and		2.02
	supervision		
			0.36
ixed costs excluding capital charges			3.57
	70 per cent of operating labour and		
	Support visitors		0.83
	6-2/3 per cent of investment per year		3.86
LOCAL GENER AND INSULATICE	I-1/2 per cent of investment per year		87
			5.56
	TUTAL CUSE OF MANUFACTURE		32.47

trialized country. These longer periods of time increase costs, both in the form of added interest on the working capital involved and due to necessity of supporting the staff associated with construction for this longer period of time.

A third factor adding to cost in less industrialized areas is the substantially higher transportation costs nocessary for the equipment which cannot be fabricated in the country.

The influence of labour costs on the total cost of manufacturing can be substantial. In developing countries, wage rates are generally very much lower than in the more industrialized countries, and this on the surface would be expected to bring about some reduction in the manufacturing cost of ammonia. However, the number of workers employed in a plant is generally much higher than would be found in a comparable plant in an industrialized country. Furthermore, the overheads associated with this labour force, such as en-site housing, companyprovided mosts etc., will add substantially to the total labour costs which in many of these developing areas will actually be greater in total than in a more industrialized area.

Unfortunately, the several variables which can affect costs often work together to result in substantially increased ammonia manufacturing costs in developing countries. Markets are generally limited and the plants that can be justified by these domestic markets are often considerably smaller than larger plants now being built in industrialized countries. Extremely low cost raw materials are generally unavailable in the developing countries, while plants which can be located in such petroleum producing areas as Kuwait or Libya would have extremely favourable costs in this connexion. Finally, the added cost of construction and operation inherent in meany of the developing countries will add materially to the manufacturing cost.

As an example of the possible variation in cost under widely differing situations, we have prepared estimates of the manufacturing cost of an extremely large ammonia plant based on low-cost natural gas in a petroleum producing country (case A) with a smaller plant based on naphtha built in a relatively unindustrialized developing country (case B). These comparisons arc shown in table 7.

In estimating the cost of these plants, we have made several assumptions, in addition to the basic variations in the cost of raw materials. The total investment in the case B plant was calculated as 20 per cent higher than a plant of equivalent size in an industrialized country, and as 5 per cent higher in case A. In both cases, operating labour and supervision pay rates were adjusted downward to reflect lower wage scales, but a larger operating staff was assumed. Labour and plant overheads were also increased in line with the substantially higher charges usually found in this category. The labour force was assumed the same in both cases, in spite of the wide difference in plant capacity.

In addition to calculating the total cost of manufacture we also show the margins for each of the two plants that would return 30 per cent on investment before taxes. This margin would include taxes, profit, and general corporate overhead. Thus we see a potential f.o.b. price, on the basis of a 30 per cent return on investment, of \$28.80 per short ton of ammonia in a large petroleum-producing country versus a \$52.57 price in a plant in a developing country. This illustrates quite well the potential advantage which very large plants constructed in areas where low-cost natural gas is available may have over plants in developing countries.

Recently developed techniques now permit the bulk shipment of anhydrous ammonia in large refrigerated tankers. The cost of transport by this method is higher per ton of nitrogen equivalent than the shipment of solid products. However, the differences are not so great as to rule out the possibility that it might be highly advantageous from the cost point of view to produce low-cost ammonia in a relatively favourable manufacturing situation and ship this ammonia by tanker to the country of consumption, where derivative products could be manufactured. It has been estimated that the cost of transporting ammonia on a 7,000 mile ocean voyage would amount to about \$12.90 per ton of ammonia. This cost of transport is substantially less than the

Process: Size: Raw material: Fixed investment:	High-pressure 1,000 tons per Natural gas \$14.7 million ( annual ton)	day	High-pressure reforming 200 ions per day Naphtha \$5.4 million (\$77.10 per a nual ton)			
Variable costs	\$	\$				
Natural gas at 5¢/MM BTU	1.55					
Naphtha at 0.9¢/1b	8.61		15.35 9.34			
		10.16		24.69		
Semi-variable costs						
Operating labour, supervision	0.41		2.06			
Maintenance	1.47 0.33		2.70 1.65			
		2.21		6.41		
Fixed costs						
Depreciation at 6-2/3 per cent of in- vestment	2.79		5.13			
cent of investment	0.63		1.15			
Plant overhead	0.41		2.06			
		3.83		8.34		
TOTAL COST OF MANUFACTURE		16.20		29.44		
Margin to return 30 per cent of inves-		12.40		23.13		
<b>F.o.b. price</b>		28.80		<b>59.5</b> 7		

TABLE 7. COMPARATIVE AMMONIA COSTS

• To allow for income tance, profit, units expenses, and general administrative expension

\$23.77 difference in price shown in table 7. Thus on a straight cost basis there would appear ample justification for such import.

Nevertheless, foreign exchange requirements would be higher in the cases of imported ammonia, since, unless special barter arrangements were possible, the entire price of the imported ammonia would be payable in foreign exchange. In the case of domestic production, only a portion of the costs would require foreign exchange, including those associated with construction costs such as imported equipment and construction supervision, and such components of operating costs as raw materials and spare parts. Therefore, generalizations on the relative cost of manufacture must be tempered by the particular foreign exchange requirements applicable in a given developing country situation. Furthermore, the very natural desires on the part of the developing countries to erect their own manufacturing plants where possible would lean towards the choice of a domestic plant even though absolute cost considerations show this to be at a substantial disadvantage.

While it is therefore possible on the basis of foreign exchange limitations and national industrialization programmes to justify plants which might be at a disadvantage with more efficient plants elsewhere, the magnitude of the disadvantage, as shown in the illustrations cited, is sufficiently large that import of this important fertilizer raw material should certainly be given at least preliminary consideration, since the effect of such a low cost could be substantial in reducing the price of fertilizer within a given developing country. Furthermore, the additional costs often associated with plants constructed and operated in developing countries would suggest that every effort should be made to minimize unnecessary costs, by way of government policy in facilitating the rapid construction of the plants, and the elimination or burdensome rules and regulations which tend to increase the cost and delay completion.

Summarizing the various changes in the petrochemical manufacture of ammonia with particular relevance to the implications for developing countries, we see a rapid shift towards the use of petroleum feed-stocks as a source of ammonia with particular emphasis on naphtha as a preferred low-cost material. The increasing availability of naphtha generally should permit many developing countries to erect sufficient plants based on this raw material.

At the same time, we may expect to see the construction of a substantial number of very large-sized plants in the more industrialized countries and in petroleum producing countries, with associated low manufacturing costs. These will increasingly put the smaller plants that may be constructed in developing countries at a price disadvantage and may suggest the desirability of importing ammonia to manufacture further derivatives. The construction of increasing numbers of tankers for transport for anhydrous ammonia in bulk will make such ocean transport of ammonia increasingly feasible.

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## 3. ECONOMICS OF AMMONIA PRODUCTION IN THE DEVELOPING COUNTRIES

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#### I. INTRODUCTION

At a recent symposium held in Augusta, Georgia, United States, 6-17 April 1964, on the subject, "The New World of Agriculture", several papers were presented which indicate an urgency in meeting the food requirements of our planet. At the present time there are over 3 billion people living on this planet, and over 2 billion of us are living on a diet which is barely sufficient to maintain us in moderate health. By the year 2000 it is expected that there will be over 6 billion of us who will have to be provided with adequate food. Some scientists strongly advise satisfying the hunger of the people by the following methods: (a) making use of as yet unutilized animal and vegetable proteins, (b) cultivating by revolutionary means edible living organisms in non-soil media; (c) synthesizing food material from inorganic raw materials. However, Mr. Jan Bauderwijn, Chairman of the Fertilizer Industry Advisory Panel of the United Nations, author of Freedom from Hunger Campaign advises us to concentrate our present efforts on increasing world food production by more intensive application of chemical fertilizers.

A conservative estimate shows that one ton of plant nutrients (N-P-K) can produce an average of ten tons of basic food. One ton of basic food provides approximately 5,000 calories per day for one year. Based on the average world intake of 2,400 calories a day per person, one ton of basic food provides enough calories for two people to live on for one year. Consequently, one ton of plant nutrients (N-P-K) provides the food for at least twenty people.

Mr. Bauderwijn estimates that by the year 2000 the world will consume 100 million tons of plant nutrients. At the present time (1961/62), the world production of N, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O totals 31.3 million tons. But very few countries have achieved a high level of fertilizer application. The average fertilizer consumption in the Netherlands, according to the FAO 1962 Review, is 215 kg N., 108 kg P<sub>3</sub>O<sub>5</sub> and 133 kg K<sub>2</sub>O, or a total of 556 kg per hectare. In Japan the equivalent figure is 312 kg per hectare, and in Belgium, it is 360 kg per hectare.

Take, for example, the nitrogen production and consumption, and the *per capita* and per-acre nitrogen consumption of twenty-five selected countries, as listed in table I. The more industrialized countries are also the countries consuming more nitrogen fertilizers *per capita*. The western European countries, the United States, China (Taiwan), Japan and the United Kingdom are in the upper consumption range --i.e., over 8 kg N per capita. Developing countries like the Republic of Korea, Peru, and the United Ar ib Republic are in the medium consumption level of 3 to 8 kg N per capita. India, the Philippines and the developing countries of Latin America are in the lower level of consumption of 0.5 to 3 kg N per capita. The consumption of nitrogenous fertilizers in the world as a whole was 3.2 kg N per capita in 1961, with P<sub>3</sub>O<sub>5</sub> and K<sub>3</sub>O consumption also, oddly chough, at about 3.2 kg per capita. In order to raise these figures to a conservatively desirable level of about 6 kg N per capita, even at the present world population level, an estimated investment in plant facilities of about \$12 billion would be needed (1).

The need for nitrogenous fertilizers is well understood in India, Indonesia, Iran, Pakistan, and some other countries. Great efforts have been made in recent years to create large production facilities. However, it will take much more investment capital and time than has so far been planned to bring these heavily populated countries to the required level of self-sufficiency in nitrogen fertilizers.

The manufacture of nitrogen fertilizers is a capitalintensive industry in that the percentage of fixed charges (which includes 10 per cent of plant investment costs for depreciation and 10 per cent, to cover insurance, taxcs and interest on capital) in the total manufacturing costs of, for example, ammonia or urea is in the order of 35 per cent to 45 per cent. Thus any improvement in the basic process which tends to reduce investment has a big impact on the cost of production. Because of significant improvements in fertilizer processes, the cost of production of basic fertilizers like ammonia and urea have shown a downward trend.

## II. BRIEF DESCRIPTION OF VARIOUS INDUSTRIAL METHODS FOR AMMONIA PRODUCTION

Ammonia is produced commercially by reacting hydrogen and nitrogen over a catalyst under pressure (300-500 atmospheres) at elevated temperatures (450°-580°C) according to the following equation:

$$N_{s} + 3H \rightleftharpoons 2NH_{e}$$
 (I)

While the nitrogen required for the synthesis gas is obtained from air, the hydrogen is derived from chemical reactions involving carbonaceous fuels, such as wood, 
 TAPLE 1. NITROGEN FERTILIZER PRODUCTION AND CONSUMPTION IN VARIOUS COUNTRIES IN THE WORLD

 In thousands of Metric Tons of Contained Nitrogen (in order of per capita consumption)

····	Production 1961/62	Consumption 1951/62	Population millions July 1960	Consumption kg. nitrogen per capita 1960/61	Consumption kg. sicrogen per hectare arable land, 1960/61
Denmark.	Nil	133.6	4.58	27.0	
Netherlands	435.4	242.9	11.5	19.5	44.5 215.2
United States.	2,936.C	2,903,0	180.7	15.1	
Norway	285.4	49.8	3.59	13.3	14.8 59
France	774.3	624.7	45.5	12.4	÷-
Federal Republic of Ger-			45.5	12.4	26.4
many	1,113.8	621.4	55.6	11.1	70.5
Belgium	262.3	103.2	9.15	10.9	72.3
Czechoslovakia	144.1	-146.2	13.7	10.9	105.9
China (Taiwan)	65.0	121.8	10.6	9.7	26.9
Spain	137.5	327.2	30.1	9.7	120.0
Poland.	281.8	-274.0	29.7		13.4
Jnited Kingdom	465.6	496.4		9.1	16.9
apan	1,088.6	695.2	52.5 93 2	8.8	63.3
ortugal .	54.9	68.4		8.1	124.0
Rep. of Korea	34.1	214.0	8.92	7.2	15
			24.7	6.9	104.7
	688.7	346.7	49.4	6.7	21.0
	31.2	42.3	10.9	6.4	28.1
Jnited Arab Rep.	106.5	191.9	25.9	6.2	71.2
1000	286.0	<b>*90.6</b>	17.9	3.6	2.2
	940.0	859.0	214.4	3.6	3.4
	12.0	55.1	65.7	1.0	3.5
hilippines	7.4	54.7	27.5	0.9	6.3
akistan	24.2	52.1	<b>92</b> .7	0.8	2.5
ndia •	109.9	<b>*28</b> 3.1	432.6	0.5	1.8
hina (mainland).	Na.	200.0	646.5	0.3	1.9

SOURCES: FAO, Fertilizers (1962),

N.a. - not available. • 1960-61 figures.

lignite, coal, natura<sup>1</sup> gas, naphtha, fuel oil and crude oil. Some hydrogen is obtained from electrolysis of aqueous solutions such as brine or caustic potash. Basically, the process steps in the production of ammonia are: (a) gas preparation; (b) gas purification; and (c) ammonia synthesis. At present there are five routes for gas preparation which have commercial importance. They are: (a) steam reforming; (b) partial oxidation; (c) water gas production; (d) electrolysis; and (e) extracting hydrogen from petrolcum refinery gases or coke-oven gases (see figure I). Of these, the steam reforming and partial oxidation have the greatest future potential for providing synthesis gas for ammonia manufacture.

# A. Gas preparation processes

Since the Second World War the trend has been away from the use of solid fuels which involves high costs of maintenance and material handling. It is interesting to note that an ammonia plant built in India in 1945 using wood from the forest was recently scrapped and replaced by a plant utilising the partial-oxidation of naphtha for gas preparation. Naphtha was chosen as the raw material because of lack of natural gas. During the last ten years, the world-wide trend has been to use natural gas, where it is available in sufficient quantities. Natural gas is converted to a hydrogen-rich gas by a catalytic process, the socalled "Gas Reforming Process", according to the chemical reaction:

$$CH_4 + H_3O \rightleftharpoons CO + 3H_3$$
 (II)

This operation is followed by a "shift reaction" in which the carbon monoxide is converted to more hydrogen according to the reaction:

$$CO + H_s O \rightleftharpoons CO_s + H_s$$
 (III)

About 81 per cent of the United States production of ammonia used the natural gas-reforming route. Other routes of gas preparation used in the United States are through the use of coke-oven gas, petroleum refinery gas, acetylene off-gas and by-product hydrogen from electrolysis of brine.

## B. Gas reforming processes

The standard gas-reforming process is based on the reaction between methane and steam at 750°C and 1-2 atm. pressure. In 1955 the pressure used in the refor-

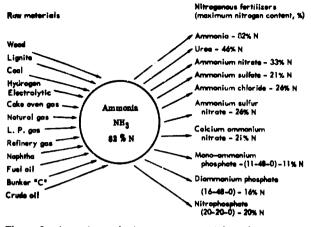


Figure 1. Ammonia production — raw materials and nitrogenous materials

ming operation was increased to about 8 atm. at an ammonia plant designed by Chemico for Escambia Chemical Company in Florida. Late in 1960 a Chemicodesigned reforming installation, operating at 18 atm. went into operation at Toulouse, France (2). Recently Chemico and Foster Wheeler (3) have installed reformers operating at 21 atm. The new plants under construction in the USA and United Kingdom use gas or naphtha reforming at 28-32 atm.

The high pressure reforming process provides significant savings in the production cost of ammonia (4). This is illustrated in table 2, based on a specific example. The advantages of the use of higher pressure are:

(a) The product gas from the reformer is at a higher pressure, reducing the compressor horsepower necessary to raise the gas to synthesis pressure;

(b) Natural gas, which is generally available at high pressure, can be directly utilized without letting down pressure;

(c) Better heat recovery from steam-condensate of the process gas is possible at the higher level;

(d) Equipment and piping of smaller size can be used;

(e) The CO converter is more efficient at the higher pressure;

(f) The  $CO_s$  removal system is more efficient and compact.

The disadvantage of higher pressure is unfavourable methane-steam reaction equilibrium. However, this has been overcome by the use of higher temperatures in furnaces. New techniques have been developed to cope with engineering design problems at these high pressures and temperatures.

## C. Liquid fuel processes

A significant advance has been the development of the partial-oxidation process. In this process, hydrocarbons are oxidized under pressure in a flame reaction, with either pure oxygen or oxygen-enriched air, to produce a gas containing hydrogen and carbon oxides. This conversion, shown in equations IV and V, is a non-catalytic reaction conducted at pressures up to 32 atm. (5).

#### TABLE 2. COMPARISON OF UTILITIES CONSUMPTION FOR NATURAL GAS-REPORMENG PROCESSES AT THREE PROSURES \*

Basis: 200 ton per day ammonia plant

(Assuming no air-preheater is used. Three alternate pressure levels)

	7.8 atm. (100 paig.)			atm. ( poly.)	17 atm. (290 paig.)		
	Quest.	\$/hour	Quan.	\$/hour	Quan.	\$/how	
Power (total kWh to compress syn- thesis-gas to \$83 psig. only) (cost: 7 mills per kWh)	3,846	26.92	3,589	25.12	3.294	23.06	
Boiler feedwater (gpm. at 220°F) (cost: \$0.001 per gal.)	101	£ 06	106	6.37	112	6.71	
Steam (net export) credit (cost: 30.60 per 1,000 lb)	1,100	0.66	(1,300)	- 0.78	(2,000)	1.20	
Cooling water, gpm (cost: \$0.02 per 1,000 gala.).	<b>4,60</b> 6	5.53	4,214	5.05	4,160	4.99	
		39.17		35.76		33.50	
Puel (nat. gas at 30¢ per 1,000 ft <sup>s</sup> ) in mole/hr.	230	26.25	244.1	27.85	258	29.45	
Total production cost per hour for synthesis gas at 883 paig		65.42		63.61		63.01	

\* These figures are for illustrative purposes only and are based on a specific design for an everages plant built in 1997.

$$4CH_4 + 2O_2 \rightarrow 4CO + 8H_8 \qquad (1V)$$

$$C_xH_y + x/2O_x \rightarrow xCO + y/2H_x$$
 (V)

There are a variety of partial-oxidation processes available: Texaco, Shell, Koppers-Totzel, O.N.I.A. and others (6). The important advantage of the partial-oxidation process is its feedstock flexibility. It can handle gases, liquid fuels up to Bunker C, or even solid fuels and frees the ammonia plant from limitation to the availability of raw materials. Many countries without adequate natural gas resources have adopted the partialoxidation process for their ammonia manufacture using liquid fuels, often imported.

Both the Texaco and Shell processes operate at pressures of about 32 atm. More recently, the Texaco process has been adapted to operate at a pressure of as high as 82 atm. The subsequent steps of CO conversion and CO<sub>2</sub> removal can be also operated under these high pressures with better efficiencies in more compact and less costly equipment. Compression costs for the CO<sub>2</sub> and CO removal are reduced.

The principal disadvantage of the partial-oxidation process has been the necessity of a low-temperature separation plant to produce the pure oxygen needed for the process.

## D. Naphtha reforming processes

There are several naphtha reforming processes which have been developed recently. The Imperial Chemical Industries Ltd. has a naphtha reforming process which uses steam and naphtha in the primary reformer followed by air addition to the secondary reformer (1), while the Chemico naphtha reforming process is a one-step process in which air, steam and naphtha are simultaneously reacted in a single catalytic-reformer unit. Both these processes operate at pressures of 22-28 atm. which reduces the power requirements for the ammonia plant. Higher pressures are restricted only by the strength of hightemperature alloys. Since the steam reforming process using naphtha has lower investment and operating costs than the partial oxidation alternate, the naphtha reforming processes could displace the latter as a means for ammonia production in many countries where naphtha is in excess supply compared with natural gas. The cost for the naphtha reforming plant is reported to be about 15 per cent higher than a natural gas steam reforming plant of the same capacity (7).

#### E. Future trends

Some of the process routes for gas preparation, with further technological improvements, may become economical in the future. They are : (a) the use of internal combustion engines to produce ammonia synthesis gas along with directly usable power (8), and (b) the use of atomic energy to supply endothermic heat for reforming reactions.

#### F. Gas purification processes

The gas produced by the methods outlined above usually contains a high proportion of CO which is converted into  $H_1$  and  $CO_2$  by the water-gas shift reaction. After that the  $CO_2$  is removed and finally the gas is cleaned to give a total carbon-oxides content of less than 10 ppm. Recent developments in CO conversion relate mainly to catalysts of improved activity while operating at a lower temperature. Such catalysts have been developed by Svenska in Europe, Girdler Catalysts and Catalysts and Chemicals, Inc. in the U.S.A, (9). Since the CO conversion equilibrium yields lower CO a lower temperatures, CO removal is more efficient with these newer catalysts which operate at lower temperatures. Changes in CO converter design (10), as well as the use of heater saturator towers (11) in tandem with the converter, are incorporated in ammonia plants built recently.

With the development of the new catalysts, the iraditional two-stage CO conversion step with two CO<sub>2</sub> removal units has been replaced by a single converter but using two catalyst beds with interquench, followed by one CO<sub>2</sub> removal unit. This results in considerable savings in investment and utilities such as steam, electricity and cooling water. With the advent of higher activity COoxidation catalyst, the CO content of the gas entering the final clean-up stage fell from 3 per cent to about 0.6 per cent.

## G. CO; remova!

There have been several process advances in CO. removal in the past decade. The cold water scrubbing process, which requires high water circulation rates, gave way to the more efficient and compact monoethanolamine (MEA) absorption system. High steam consumption and corrosion problems were some of the earlier disadvantages of the MEA system. The introduction of the hot carbonate system by Chemico for the first time in 1955 at the Escambia plant proved the superiortity of this process. It was particularly effective on the natural gas reforming process, and since steam and cooling water requirements were lower, a reduction in the size of the heat-exchanger equipment was effected. Next came improvements in the hot carbonate system which includes the Giammarco modification using an arsenic additive and the Catacarb process using an undisclosed non-toxic additive. Both these processes claim to produce lower CO<sub>2</sub> content in the treated gas. They also claim lower liquid circulation rates and smaller energy requirements than the original hot carbonate process. As noted earlier, the changes in CO conversion technology have brought the MEA system back into favour. With the adoption of high pressure gas reform processes and the singlestage CO-converter, heat economy is better with a single MEA system than with the potassium carbonate system. Some new solvent processes are also being developed by Fluor, Shell and Hydrocarbon (12), but none of these seem to have been operated on an industrial scale yet. An excellent review comparing the economics of several alternate CO<sub>2</sub> removal processes has been made by J. Jennett (13),

## H. Final clean-up of CO and CO,

Final clean-up of synthesis gas to remove CO and CO<sub>8</sub> to less than 10 ppm was originally accomplished with the classic copper-liquor process. This process had the drawback of higher maintenance costs because of corrosion problems involved in the use of ammonical copper solution at high pressure. In addition, the users of this process have been involved in the serious problem of stream pollution in the neighbourhood of the plant. Therefore, the alternate process of methanation becomes economically attractive. In the methanation process, both CO and CO<sub>2</sub> are reduced to less than 10 ppm by conversion to methane over a nickel catalyst according to equations VII and VIII.

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$
 (VII)

$$CO_1 + 4H_1 \iff CH_4 + 2H_2O$$
 (VIII)

The methanation process, originally used only ultra high pressure synthesis processes (Clrude, Casale) (14), has now been adopted by medium-pressure synthesis processes and has almost completely replaced the copperliquor process in ammonia manufacture. The loss of valuable hydrogen as methane and the higher purge losses of ammonia with higher inerts in the gas, are the principal disadvantages of the methanation route. They are more than offset, however, by other advantages of the methannation step such as low investment cost, low operating cost and simplicity of operation.

In plants employing oxygen as a process raw material, liquid nitrogen from the air-separation plant is used for the final clean-up of synthesis gas of its CO and CH<sub>4</sub> content. This is also the case for ammonia plants using the off-gas from a partial oxidation acetylene plant as the foedstock for production of synthesis gas. This method of CO removal is known as "nitrogen wash".

#### 1. Ammonia synthesis

Although no new process has been introduced for ammonia synthesis in the past decade, the trend has been towards adoption of the moderate pressure processes operating at 300 to 350 atm. Such processes as Kellogg, Chemico, and Fauser are preferred over the higher-pressure processes of Claude and Casale operating in the range of 600 to 1,000 atm.

#### J. Catalysts

The only improvement in the catalyst was the introduction of the triple-promoted iron oxide catalyst by Cyanamid and Topsoe. This improvement while helpful has had a minor marginal effect only, since conventional catalyst is already a highly efficient material.

### K. Converter design

Some intrinsic changes in the mechanical design of the converter have been introduced which result in better temperature control or better steam economy. Chemico's converter has been modified to include a triple-tube in the catalyst-basket design. The middle tube acts as an insulator to even out the temperature profile in the catalyst bed (15). Another step forward was the use of a steamrecovery system either inside or outside the ammonia converter to utilize the sensible heat of the product gas. Both Montecatini and Chemico have installations in operation which produce by-product steam from the converter. The steam produced (up 0.95 tons of steam at 250 psig per ton of ammonia) results in a significant reduction of ammonia production cost, particularly in areas of high steam cost (16).

#### L. Compressor design

Improvements in compressor ...esign also have kept pace with ammonia technology. The compressors with integrated services including air compression, recycle gas pumping and make-up gas compression, help reduce the cost of compressors and associated piping in the ammonia plant. The recently developed large capacity centrifugal compressors for the compression of synthesis gas has led to considerable changes in the technological schemes for large production units of 500-600 T/D, resulting in consi' ble change in the economics of ammonia production..

#### M. Converter capacity

The size of the ammonia converters has increased from the 120 tons per day prevailing in 1950 to 600 tons per day capacity since 1962. Both Kellogg and Chemico have recently designed converters with capacities of 600 tons per day. Thus the capacity of the converters has increased 500 per cent in the past twelve years, and a converter with a capacity of 1,000 tons per day is on the drawing boards now. The great impact of the higher converter capacity is felt in the lower operating costs, including utilities, maintenance, etc. Both the mechanical engineer and the metallurgist have aided the chemical engineer in this accomplishment. A similar trend is also neted in larger single-units for gas reforming, gas purification, etc.

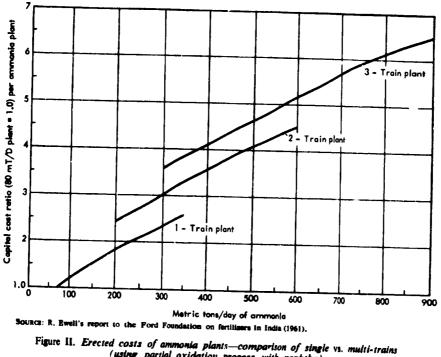
#### III. THE COSTS OF AMMONIA PRODUCTION

The advantages of larger capacity single-train plants in preference to multi-train plants is illustrated in figure II which shows comparative costs of battery limits ammonia plants at various capacities. Lack of flexibility in operation and maintenance in a single-train plant is overcome by using spares for critical rotating equipment like compressors, pumps, etc., or by using two units of each rotary item with 60 per cent rated capacity.

As indicated in figure II, the cost of an ammonia plant is not a rigid figure. Its actual value depends on many factors such as the designed rating, the number of trains to make up the rated capacity, the type of raw material available, the process selected, the distance over which the plant equipment has to be transported, and the cost of erection labour.

In building ammonia plants in developing countries, it is usually necessary to allot a larger portion of the investment to yard facilities and utility accessories than that commonly allowed in highly industrialized countries.

It is of course not advisable to make estimates without knowing the details of local conditions. All that can be said as a guide is that a plant producing 200 metric tons of ammonia per day may cost in the order of



(using partial oxidation process with naphtha)

Basis: Erected cost of 80 m.T/D ammonia plant using naphtha partial oxydation is 1.0.

\$50.00 to \$75.00 per annual ton capacity, depending on the factors just mentioned, on battery-limit basis.

Likewise, the manufacturing cost is dependent upon many factors largely local in nature. Of course, the major item in the manufacturing cost is the cost of raw materials. This item could account for 25 to 50 per cent of the total cost depending upon the kind of raw material and its price.

When operating very large single-train units on natural gas the cost of production can be very low indeed. A figure of \$24.00 to \$25.50 per metric ton of ammonia has been given, based on the cost of natural gas at \$0.20 per million BTU.

When the ammonia plant is of a moderate capacity, the manufacturing cost will not be that low. When raw materials other than natural gas are used, the cost will be higher than in the case of natural gas. Recent estimates  $(1\overline{7} \ 18)$  give the manufacturing cost of ammonia as \$39.00 to \$40.30 per metric ton based on naphtha-steam reforming at a plant capacity of 120,000 metric tons per year (see also table 3).

## IV. ECONOMICS OF AMMONIA MANUFACTURE IN THE UNITED STATES OF AMERICA

The current capacity of the anhydrous ammonia plants in the United States (figure III) as of 1 January 1964 is 7.6 million tons distributed among eighty-seven individual plants operated by fifty companies. By the end of 1964,

the total capacity will reach the level of 8.7 million tons per year. Enough new ammonia plants have been planned to push the total to over 10 million tons by 1967. Of this total capacity, 81.2 per cent is based on natural gas as the raw material, 10.9 per cent on petroleum refinery gas, 5.2 on by-product hydrogen from chlorine cells, 1.5 per cent on coke-oven gas and 1.2 per cent on fuel oil, as of 1 January, 1964.

Although the new plants are very large single-train units, the majority of the ammonia plants in the United States are of medium size. The capacity of individual units of the plants built during the Second World War did not exceed 75 T/D. The Korean War brought into being units of 150-200 T/D capacities. Only rather recently have the individual capacity of the converters been increased to 300-400 T/D, and now these converters are operating at 600-700 T/D and the latest developments is to use converters of over 1,000 T/D.

In spite of these very attractive economics for the production of ammonia in large single-train units, the smallsize ammonia plants (60-100 T/D) are still being built in the United States. The main justification for such small units lies in the fact that small units serve to meet local needs which otherwise can only be met by paying expensive transportation costs.

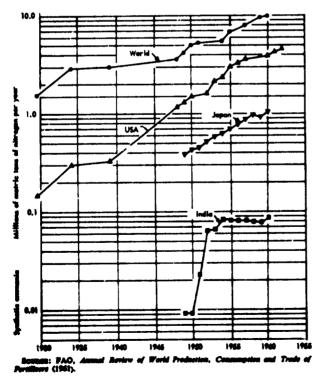
Due to the steady advancement in the technology of ammonia manufacture in the United States, the price of ammonia on the open market has been very steady while prices of other commodities had risen appreciably (see

TABLE 3. AMMONI	A PRODUCTION COS	T PER	SHORT	TON O	r NH <sub>s</sub>	¥S.	PLANT	SIZING

Tons/day

	· · · · · · · · · · · · · · · · · · ·	60 T	1001	<b>200 T</b>	300T	400T	600 T
1.	Natural gas/ton 31,000 SCF at 20 ¢/cu ft	6.20	6.20	6.20	6. <b>20</b>	6.20	6.70
2.	Operating labour cost 4 men/shift + 1 supervisor (\$3/hr)	6.00	3.60	1.80	1.20	0. <b>90</b>	0. <b>60</b>
3.	Plant overhead, management, fringes, etc. 100 per cent then 2	6.00	3.60	1.80	1.20	0.90	0, <b>60</b>
4.	Electric power 625 kWh at 8 ¢/kWh	5.25	5.00	4.80	4.80	4.80	.44
5.	Cooling water 48,000 gals $\Delta T = 32 \text{ °F at}$ 2¢/M gals	1.00	1.00	1.00	1.00	1.00	1.38
6.	Make-up and boiler feedwater at 8¢/M gal	.05	.05	.05	.05	.05	.05
7.	Maintenance costs at 21/2 to 3 per cent of capital investment	2.60	2.10	1.75	1.45	1.25	0.90
8.	Taxes (real estate at 2 per cent battery limits capital investment)	1.80	1.60	1.40	1.15	1.00	0.70
9.	Interest at 5 per cent on capital cost (1st yr. basis)	4.30	4.20	3. <b>50</b>	2.90	2.00	2.10
10.	Amortization at 10 per cent a yr	9.00	8.00	7.00	5.75	5.00	4.20
	TOTAL	42.20	35.35	29.60	25.70	23.60	17.67

Note : These prices are based on natural gas cost of 20  $\neq$  per l million BTU. For production costs based on natural gas other than 20  $\neq$  per million BTU (see figure IV).



Pigure III. Production of synchotic anumonic in metric tons of nitrogen

table 4). This steadiness of price is currently pointing to a downward trend as more ultra-large-size ammonia plants are now under construction and still larger ones are being planned.

## V. ECONOMICS OF AMMONIA PRODUCTION IN OTHER INDUSTRIAL COUNTRIES, JAPAN AND WESTERN EUROPE

Before discussing the economics of ammonia manufacture in developing countries it is valuable to take a glance at the economics of ammonia production in the highly industrialized countries other than the United States, Take Japan, for example. Japanese agriculture depends heavily on chemical fertilizers. Its demand for nitrogen is not much below that of the most intensive consumer, the Netherlands. In spite of the fact that the Japanese Islands have not been endowed by nature with large deposits of natural gas and petroleum, the Japanese productive capacity for fertilizer nitrogen which is mostly ammonia and its derivatives is exceeded only by the United States, the Federal Republic of Germany and the USSR (fig. III). In 1963/64, Japan's production of nitrogen was about 1,400,000 metric tons compared with the following : USA 5,000,000 metric tons, Federal Republic of Germany 1,600,000 metric tons and USSR 1,500,000 metric tons. Recent news from Japan shows that in spite of a large excess of ammonia capacity over the domestic no there are new programmes underway for further expansion

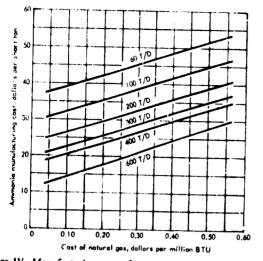


Figure 1V. Manufacturing cost of ammonia made from natural gas at various single-train capacities

of manufacturing facilities. Up until now, the Japanese ammonia industry has been based primarily on the use of individual units of 50-200 T/D. But the new programme calls for single units of 500 T/D and larger. Only in the last decade have the Japanese ammonia plants been gradually switching from solid fuels such as coal, coke and lignite to natural gas and liquid fuels. The relatively small reserves of natural gas have forced the Japanese to use liquid fuels imported from abroad. Partial oxidation processes, described above, have permitted the Japanese to use crude petroleum as the raw material for making ammonia. Besides crude oil, Japan can use the certain products and by-products of the oil refining industry such as naphtha and by-product hydrogen. In this particular case of naphtha, the recently jeveloped steamreforming process will be very useful.

Until the Second World War, the manufacture of ammonia in European countries in both the West and the East was primarily based, with but a few exceptions, on the use of solid carbonaceous fuels. At that time there were already, however, a few plants in which the by-product methane was converted to hydrogen via the steam reforming or other cracking processes. In Norway and Italy certain amounts of ammonia were obtained from electrolytic hydrogen. The discovery of huge deposits of natural gas in Southern France, in the Po Valley in Italy and more recently in the Netherlands has now induced the synthetic ammonia industry to switch over from solid fuels to natural gas as the basic raw material for the generation of hydrogen. This real revolution in the fundamental economics of this important industry is obviously controlled by the more advantageous economics of producing ammonia from natural gas. The same pattern takes place in Japan where, however, the lack of large deposits of natural gas is compensated to a very large extent by the use of imported crude oil and the by-products of the oil refining industry. In France nearly 50-60 per cent of the ammonia in 1963-64 are being produced from non-solid fuels. By 1968 over 90 per cent will be made from gas or liquid fuels. The

same is true for Italy. Under such circumstances, it is relatively obsolete to present the economics of the production of ammonia from solid fuels.

However, it is to be noted that in the Federal Republic of Germany the ammonia industry is still tied very strongly to coal and lignite. In the Netherlands up until the present time ammonia is largely produced from coke or coke-oven gas. This is also true for Belgium. In all of these countries the arrival of natural gas has not necessarily been followed by the reduction of the consumption of solid fuels. In order to allow the solid fuels to maintain their present position, the price of natural gas supplied to the ammonia industry is artificially equated to the price of the solid fuels. For instance, in the Netherlands it is maintained at a level of about 50 ¢ per 1 million BTU, while in Texas and Louisiana the gas is priced at 20 ¢ and less per 1 million BTU. This pricing in the Netherlands is definitely dictated by a desire to maintain the coal industry at a competitive level.

In a very recent study for  $\approx 1,000$  T/D ammonia plant in the Netherlands, the operating cost of ammonia seems to be obtainable at a level of \$32.00-\$35 per ton on the basis of 50 ¢ per 1 million BTU for natural gas. This compares quite advantageously with older plants in which the cost of ammonia produced from coke or cokeoven gas was, and still is, over \$50.00 per ton.

# VI. ECONOMICS IN THE DEVELOPING COUNTRIES

## A. Agricultural requirements

Dr. F. W. Parker, the retired Assistant Director-General (Technical) of the Food and Agricultural Organization indicated in 1962 that more than one-half (52 per cent)

TABLE 4. AMMONIA PRICES IN THE UNITED STATES (FERTILIZER GRADE ANHYDROUS AMMONIA, TANKS, WORKS, FREIGHT BQUALIZED, EAST OF THE ROCKY MOUNTAINS, 1950-1963) \*

•		price \$U.S. 1,000 <b>16</b>	Price	Average consumer price index in the U.S (1947-49 = 100)	
Your (Jan. to Doc.)	High	Low	oguivalant 10 1930 dollar		
1950	75.10	_	75.10	102.8	
951	75.50	—	69.80	111.0	
952	79.00	79.00	71.40	113.5	
953	\$2.00	79.00	73.70	114.4	
954	85.00	\$5.00	76.10	114.8	
955	\$5.00	85.00	76.20	114.5	
956	78.50	72.00	69.30	116.2	
957	\$2.00	80.00	70.10	120.2	
958	84.00	80.00	69.90	123.5	
959	\$6.00	84.00	70.80	124.6	
960	88.00	84.00	72.00	125.4	
961	92.00	84.00	74.00	127.8	
62 (Dec)	92.00		79.40	127.0	
963 (July 15)	92.00		78.70	130.3	

\* Prices for assessments as quoted in Oil, Paint, Drug Reporter (1995-1963). These "quoted "prices do not reflect actual prices which have scenarizes been much lower in the resent years. Is some instances, the price paid for perchand scenarizes was in low as \$25.00 per doort years.

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of the world's population is under-nourished. If the present rate of growth of the population remains unchanged, the food requirements will be increased by 75 per cent in 1980 and 168 per cent by the year 2,000. For the Far East the requirements will have to be increased by 119 per cent and 306 per cent, respectively. To achieve such food supply targets the production of chemical fertilizers will have to be increased proportionately. According to FAO data, the farm output index in the USA has increased (1947/49 = 100) from 72 in 1935 to 124 in 1958, corresponding to the increase of fertilizer consumption index from 29 to 166 for the same period. World consumption of fertilizers was about 2 million tons  $(N + P_2O_3 + K_2O)$  in 1905, 9.2 million tons in 1939, 27.1 million tons in 1959/60, and 29.3 million tons in 1961/62

In the developing countries which together account for more than two-thirds of the world's population, they consume less than 15 per cent of the total chemical and commercial fertilizers whereas the more industrialized but less populous countries use more than 85 per cent. In India the future fertilizer needs were estimated at 7.28-7.6 million tons of N,  $P_nO_n$  and  $K_nO$  in 1900. It has been estimated that the fertilizer needs for the other developing countries together amount to about 40 million tons of plant nutrients per year. This compares with present use of less than 5 million tons in all the developing countries while the world's total consumption is about 30 million tons. The 40 million tons of plant nutrients per year would require staggering financial efforts to raise probably over 5 billion dollars.

Of course all this need not be achieved at once, but a start in the direction of self-sufficiency is desirable. Since ammonia manufacture is a highly technical operation, it cannot be started on too small a scale. The minimum economical size of an ammonia plant varies with local conditions, as already discussed in section 111 above. Among the developing countries, conditions regarding raw material supplies, power facilities and transportation facilities are more or less all different. But in an average case the question of a minimum economical size of an ammonia plant has been studied. At the conference on the Development of the Fertilizer Industry in Asia and the Far East sponsored by the United Nations Economic Commission for Asia and the Far East and the Dureau of Technical Assistance Operations held at Bombay, India, on 12 November to 2 December 1963, a view was expressed that a single-train ammonia plant of 125-150 metric tons per duy capacity was occasidered most economical for the developing countries. After the first ammonia plant has been installed and normal operation and preaction established, then additional facilities may be planned and executed as fast as financial resources may pormit.

## B. Availability of raw materials

There is plenty of natural gas and oil in the regions around the Porsian Gulf to satisfy the nitrogen fortilizer requirements of all developing countries. But such large potential concumers as India and China (mainland) have not been so generously endowed by nature. In the past the manufacture of a months in India had to rely on here economical types of raw materials such as coal coke, lignite and even wood, as in Travencore. The Nangal plant uses hydroelectrical power to generate hydrogen by electrolysis and low-temperature distillation of air to obtain nitrogen. New plants under construction in India will use natural gas in Assam and petroleum refinery byproducts in Trombay. The future raw materials for nitrogen fertilizers in India will probably rely more and more on petroleum and its by-produc. Most of this petroleum will have to be imported. The example of India, with its huse agricultural requirements and insufficiently developed natural resources, is not necessarily typical of all developing countries. But the study of India will lead to certain conclusions which should be of interest to most of the countries in short supply of fertilizers.

Where raw materials for making ammonia and nitrogen fertilizers are plenty, such as countries in the Persian Gulf region where petroleum and natural gas are available in almost unlimited quantities, it might be economical to build plants to make more fertilizers than are needed locally, and to export the surplus to countries where self-sufficiency has not yet been achieved. But this involves trading on the international market which will be discussed in more detail. For the moment we may note the example of Trinidad and Tobago, where local demand for ammonia is as yet non-existent but where a private company last year built a large ammonia plant with an output of 600 tons per day. Most of the product from this plant is exported to and consumed in the United States. The reason for the auccess of such a venture is the availability of a very rich supply at very low cost of a basic material, natural gas, in Trinidad and Tobago.

#### C. Training of technical personnel

Since ammonia manufacture is a highly technical operation, it requires specially trained personnel to operate and to maintain the efficiency of the plant. Training must start at the time ground is broken for the erection of the plant and continue through to several months after the plant has been actually started and producing. All this training of course costs money, but it is the only way for the developing countries to get compotent personnel.

With the assistance of the United Nations, technical personnel may be trained under less restrictive conditions than otherwise. In either case the cost of personnal training should always be a part of total investment allotted to an ammonia-pleas project, whether it be the first plant or the nth plant in a developing country. Only in the case of an expansion of an existing plant on a single site, the training of new personnal may be related.

#### D. Marketing

For developing countries where dominal furtilizers are urgently needed, there should be no problem of marketing, once the furtilizer is produced on a continuous basis. But the problem is far flows as despite as it appears to be. There is in the first place the question of comptance by the formers, which is tage will depend upon conditions under which even in the United States "the farmers must be sold." This means publicity, basic advertising, and education. There are the problems of metohing the grade of fertilizer against the type of the soil and the nature of the crop, the problem of transportation and distribution, and the problem of correct timing of delivery. All these problems must be satisfactorily solved otherwise some of the precious fertilizers would not be utilized as planned.

Even in a highly industrialized country like the United States, it took the Tenneusse Valley Anthority (TVA) several years to educate the people in the Tennessee Valley to use ammonium nitrate fortilizer. In the developing countries education and production would have to proceed side by side. Once the fortilizer is uscepted by the farmers, expansion of production would be easier than the task of building the first plant.

In developing countries where the raw materials for ammonia production are plentiful there is opportunity of exporting the surplus asymptic such as in the case of Trinidad and Tubago, already mentioned above. The Near East countries may follow this example and make large quantities of ammonia or other strengen fletilliers to be used locally as well as to export it to other countries which are not yet self-sufficient, such as Chins (Taiwan), India and Pakistan.

Such a scheme is concentically feasible if the saw materials in question, such as natural gas, maphtha, orade petroleum or petroleum rofinery gas, are in large supply and at low cost. But that is not all. Once a country wishes to export things like anomenia and mitrogen floriliser to anoth a country, that country is entering an international merhot which at once imposes a set of rigid trading conditions upon the exporter. Some of the couditions are:

- (a) Quality of product up to the established standard;
- (b) Availability of shipping facilities or agains,
- (c) Mosting specified delivery dates,
- (d) Taking part in computitive bidding.

The last condition imposes on the exporter an even more rigid condition which is that the exporter must be able to produce the commodity. e.g. ammonia, at a cost considerably lower than the importing country can produce, so as to cover the shipping cost and the import duty. This, of course, is not easy especially for the developing countries, but it has been done.

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# 4. NITROGEN FERTILIZERS AS A PETROCHEMICAL OPERATION

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## I INTRODUCTION

The approach to nitrogen fertilizer manufacture in developing countries can be divided into two basic categories, the first being represented by countries that have available adequate supplies of carbonaceous or hydrocarbonaceous raw materials, the other by those countries which, lucking these raw materials, would be forced to import either the finished nitrogen fertilizers or the necessary raw materials for their manufacture

In the latter case, it generally is not difficult to justify raw material importation when it is realized that the amount of this raw naterial required is semewhat less than one-half the weight of the amount produced therefrom, thereby effecting great sevings not only in the cost of the nitrogen fortilizer per se but also in the cest of transportation. It shoud be noted that while ammonia, for instance, might be purchased on the European merket for roughly \$49,00 per ten, the transportation observes could easily bring the total cest to the former in some distant country to as high as \$400,00 per ten, or ten times the bare cost of the ammonia (1).

Taking the hypothesioal case presented above and applying this to a developing country with a population of only ton million people we find that the difference between importing the new material and importing the functed product — while applying only therety pounds of aitrogen per capita per year — could amount to approximately \$20,600,000 per year — while it is difficult to generalize internationally, on the basis of United States of America investmence, this saving could in only one year pay for the 480 tons per day of amount manufacturing capacity required

An additional and very important advantage to installing nitrogen fortilizer menufacturing facilities in a devoloping country is the reduction in the amount of meany flowing out of the country for direct purchases of these facilities.

The installation of over a relatively small facility will result in greater fixed prediction per zero of arable land with a not reduction in purchases of enternal material and a resultant reduction of each flowing out of the unstity.

The basis building block for all stronges fortillant is annexis. The massaur is which ammedia manufactoring because a petrochemical operation will now be discussed.

## H. SOURCES OF RAW MATERIALS

Ammonia is produced commercially by the direct combination of hydrogen and nitrogen, two guesous elements. This combination occurs at high pressures and temperatures, with the aid of a catalyst.

The nitrogen required in ammonia synthesis is obtained from the air, with the oxygen being separated from the air either by combustion or by liquefaction and fractionation.

Supplying the hydrogen required for ammonia synthe is is a major part of the ammonia process, and is the part of the process that has shown the greatest diversity, both in the processes employed, and in the raw materials used as a source of the hydrogen

All of the hydrogen used in manufacturing anamonia is obtained from two sources. One is the hydrogen present in water, and the other is the hydrogen present in hydroenrisems, principally gaseous hydrocerbons such as neural and refinery gases, or isqued hydrocerbons such as prepane, butane, naphtha, fast oil, or orade oil. In a few very isolated eases, ammonia is still produced from coal and weter.

At the present time, the greater portion of the hydrogen used in ammonia synthesis is obtained by reacting hydrosarbons with steam, onygen, or mintures of the two substances.

Natural gas is the hydrosarbon most widely used in ammonia syntheses. It is being used to produce hydrogen by reacting it estalytically with steam in the steam reforming process, or by estalytic or non-catalytic reaction with onjugon and steam.

Robusty gas, which is a minute of hydrosarbon gases obtained as a by-product of oil robuing operations, is also being used as a source of hydrogen for ammonia symbleces. The same process stops may be used as in the case of untural gas.

The ass of gassees hydrosarbans as now materials for hydrogen production is at present limited to used in which down products are bring produced or are bring supplied from pipeline. The commercial transportation of figurated natural gas is now bring developed, but it is unlikely that this will because a significant second of supply of natural gas for anomalia production because of the high transportation and.

Hydrosarbons, which are accusally liquid, each as sagilishs, heavy fuel all and couds all, are being dilpped

over great distances at comparatively low cost, and are being utilized to an increasing extent as raw materials for ammonia synthesis in areas which do not have a local supply of natural or refinery gas.

The liquefied petroleuin gases, propane and butane (LPG) may also be shipped, although the shipping costs are greater than for the heavier hydrocarbons, since either pressure or refrigerated tankage is required. Consequently, these products have found limited use in ammonia production.

Petroleum naphtha, which is the name commonly given to mixtures of hydrocarbons from pentane to docane, is froquently available in substantial quantities as a relatively low-cost product of oil refining. Consequently, it has become an important raw material for the production of hydrogen for ammonia synthesis.

Two methods are presently available for the production of hydrogen from petroleum naphtha. One of these is non-catalytic partial oxidation. Several commercial processes are available at present for carrying out this operation, which may use any gaseous or liquid hydrocarbon as feedetock, and so may be used with naphtha.

The second method for producing hydrogen from naphtha is by catalytic steam reforming, similar to the process so widely used with natural gas. The use of naphtha in the steam-reforming process has been made possible by the development of special catalysts for this purpose. Several companies have developed such catalysts and are presently building plants for producing hydrogen from petroleum naphtha by the steam-reforming process.

The principal method presently available for the utilization of fuel oil or crude oil for the production of hydrogen for amnionia synthesis is non-catalytic partial oxidation. As was mentioned above, any gaseous or inquid hydrosarbon may be used for feedbrock in partial oxidation processes.

## III. COMBINED FACILITIES FOR PETROLEUM REPINING AND AMMONIA MANUFACTURING

At this point it would be well to discuss the potential advantages of installing petroleum refining facilities in conjunction with nitrogen facilities facilities. It is a wellestablished fact that the over-all economy of a nation is inenerably related, not only to that nation's ability to cope with feeding its people, but also to its ability to supply the energy required for the manufacture and transportation of humaries as well as basic necessities.

Crude petroleum offers an excellent source of both requirements. As has been shown, various hydrocarbon fractions from orude petroleum may be utilized as raw material for the manufacture of mitrogen fortilizers.

On eccession, the preliminary evaluation of available crude ells will indicate that the percentages of the various fractions are considerably out of balance with the product requirements and if expect of the surplus products is not presticable, the entire project may be abandoned. Not two long ap there was no alternative to this procedure; however, today, with the advant of modern petroleum refining technology, this is not the case. In fact, a judicious analysis of the entire project, including modern petroleum refining techniques, as well as petrochemical operations, will almost always result in the development of a potentially profitable manufacturing complex.

Today it is possible to adjust the product distribution of a petroleum refinery to almost any reasonable requirement. Most of the very powerful tools available for this adjustment are based on the relatively new processes utilizing hydrogen (2), (3). This utilization of hydrogen in the petroleum refinery is of the utmost importance if an ammonia plant is part of the over-all manufacturing facility. As has already been shown, the first unit in ammonia manufacturing facilities produces hydrogen which can be used not only for ammonia synthesis but also can be purified to supply the requirements of the hydrogen-consuming processes in the petroleum refinery.

The savings in such an arrangement are obvious. With this portion of the plant being larger, a reduction in the cost of hydrogen as well as ammonia will be effected, thereby making the entire project more attractive financially, while at the same time adjusting the petroleum refinery product distribution.

From the foregoing it can be seen that close co-ordination between petroleum refining planning and nitrogen fertilizer facility planning is essential in order that the project may approach the optimum utilization of raw material as closely as possible. Conversely, any attempt at analyzing one project without the other could very possibly result in abandonment of what actually could be a potentially attractive project.

The final products from a nitrogen fertilizer manufacturing facility will, in general, be compounds of ammonia rather than anhydrous ammonia itself. At the present time, the application of anhydrous ammonia directly to the soil is steadily increasing in the United States. However, it will probably be some time before the technical difficulties inherent in this operation can be sufficiently simplified to allow significant use on the basis of low investment required for the necessary application equipment.

In view of the many possible nitrogen compounds, it would be extremely difficult to generalize on investments for the entire complex. However, because of the une of ammonia in any of these compounds, an evaluation of the ammonia manufacturing facility alone will normally be sufficient for preliminary analysis of the entire project.

## IV. AMMENIA SYNTHEMI GAS PRODUCTION

The processes available for ammonia synthesis gas production may be divided into three basic groups. The first group is concorned with the gasification of solid cerbonaceous materials such as coal, lignite and pest. This group of raw materials is converted into synthesis gas b, use of the classical water-gas reaction which subjects the earliernate steaming for the water-gas reaction. By proper selection of sycles and with use of a gas holder for mixing it is possible to arrive at the required synthesis gas mixture required for ammonia synthesis.

In 1948, roughly 50 per cent of the nitrogen production of the world derived its hydrogen from water-gas but by 1955 this was reduced to approximately 13 per cent (4). This reduction was due mainly to the phenomenal growth of steam-hydrocarbon reforming.

Depending upon the availability of raw materials, this system still has a place in modern ammonia manufacturing, even though the investment required is much higher and in general the manufacturing costs are much higher. To illustrate the magnitude of increased investment and manufacturing costs of the solid carbonaceous material gasification, the cost of such a plant would be almost twice the cost of an equal size steam-hydrocarbon reforming plant and the total manufacturing cost would be something over one and one-half times that of a similar steam-hydrocarbon reforming plant (5).

The next group of raw materials would include heavy liquid hydrocarbons such as whole virgin crude oil on up to very heavy vacuum reduced crude. In this case, the heavy hydrocarbon materials are oxidized in the presence of a limited supply of high purity oxygen. This results in the production of hydrogen along with carbon monoxide. The carbon monoxide is reacted over a catalyst with steam to form more hydrogen and carbon dioxide. Carbon dioxide is removed by MEA scrubbing and the small amount of residual carbon oxides are removed by washing with liquid nitrogen, thus producing a synthesis gas suitable for ammonia reaction (6).

In the instances where lighter hydrocarbons are unavailable, this system can be applied quite successfully. However, due to the severe operating conditions in the partial oxidation reactors and the necessity of installing an air liquefaction plant for the supply of nitrogen, this process is also more expensive than steam-hydrocarbon reforming and also somewhat more difficult to operate.

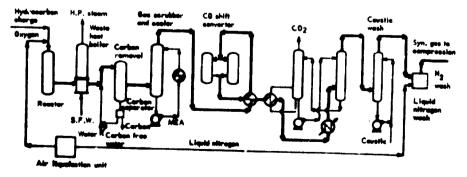
An ammonia manufacturing facility based on partial oxidation would initially cost approximately 25 per cent more than an equivalent steamhydrocarbon reforming process and, at the same time, the ammonia produced from such a unit would cost somewhat over 11 per cent more. Figure I is a simplified Flow Sheet of the synthesis gas preparation section of a partial oxidation type ammonia manufacturing facility. The third group consists of hydrocarbons ranging from naphtha through natural gas or methane. If raw material of this type is available then this is unquestionably the most economical method for manufacturing ammonia. As shown in figure II, feed gas is desulphurized mixed with steam, preheated, and then admitted to the primary reformer. Primary reformed gas, containing an appreciable amount of methane, is further reacted with air over additional catalyst in the secondary reformer, producing gas containing carbon oxides and steam, and hydrogen and nitrogen in the desired ratio for ammonia synthesis.

Condensate is added to the secondary reformer effluent and the mixture flows to a heat exchanger which preheats the feed-steam mixture to the reformer. Leaving the preheater, the gas enters the first bed of the CO converter and is then quenched with steam and condensate before entering the second bed of the CO converter. The heat content of the converted gas is utilized to preheat methanator feed and then to supply regeneration requirements for the Girbotol CO<sub>2</sub> removal system. Condensate formed in the reboiler is removed and the process gas flows to a shell and tube cooler before entering the CO<sub>2</sub> absorber. Here, essentially all of the CO<sub>2</sub> is removed by counter-current scrubbing with lean amine solution from the regeneration section.

Gas from the absorber is preheated by heat exchange with the CO converter effluent to the required temperature for the methanation reaction. The residual CO and CO<sub>3</sub> are reacted with hydrogen to form methane and water. The methanator effluent is cooled in a shell and tube exchanger before entering the synthesis gas compressors.

Rich amine solution from the absorber flows to the regeneration tower after heat exchange with the lean solution leaving the base of the tower. In the regenerator, the CO<sub>3</sub> is stripped from the solution with steam generated in the reboiler. The CO<sub>3</sub> overhead is cooled and delivered at about 2 psig. Lean solution leaving the heat exchanger is cooled in a shell and tube exchanger and pumped to the CO<sub>3</sub> absorber to complete the cycle.

The primary reformer furnace is fired with natural gas or any suitable distillate fuel. The purge and flash gases from the ammonia synthesis section are also burned in this furnace. A waste heat boiler and economizer recover heat from the primary reformer stack gas and generate the steam required for the operation of the plant (7).



Piguro I. Synthesis per preparation by partial antidation

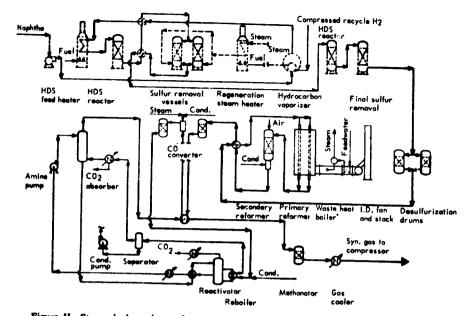


Figure II. Steam hydrocarbon reforming (supplementary equipment for naphtha feed stock is shown dotted)

## V. AMMONIA SYNTHESIS PROCESSES

Ammonia is manufactured by reacting nitrogen and hydrogen together at high temperature and pressure in the presence of an iron catalyst. Ammonia synthesis gas, containing a mixture of one volume of nitrogen and three volumes of hydrogen, is passed over an iron catalyst at temperatures of 400 to 550°C and at pressures from 100 to 1,000 atmospheres. A portion of the synthesis gas, usually between 10 and 20 per cent, is converted to ammonia. The gas leaving the catalyst is cooled to condense the ammonia and permit its recovery as liquid ammonia, while the remaining synthesis gas is recirculated over the catalyst, along with fresh make-up synthesis gas. The over-all yield of ammonia from the synthesis gas is in excess of 90 per cent and will vary alightly depending upon the purity of the synthesis gas used (see figure III).

There are more than three hundred synthetic ammonia manufacturing plants operating or under construction in the world today, ranging in capacity from about thirty tons per day to six hundred tons per day. About two-thirds of these plants operate at 250 to 350 atmospheres pressure and at reaction temperatures of 450° to 500°C, these being similar to the conditions used in the original Haber process, first operated commercially in Germany in 1913.

A smaller number of plants use operating pressures of 900 to 1,000 atmospheres, and a few are operating at pressures ranging down to 100 atmospheres.

Higher operating pressures give higher ammonia conversions per pass through the entalyst and permit liquefaction of the ammonia product by esoling the gas stream with water. However, more power is required for compression of the feed-gas mixture, and more specialized equipment is required for higher pressure operation. As the operating pressure is decreased to 200 atmospheres or less, larger refrigeration capacity is required to separate the product ammonia from the circulating gas stream, and the yield of ammonia per pass decreases as well.

The optimum choice of operating temperature and pressure for the ammonia synthesis process will depend on a number of factors, including plant size, purity of synthesis, gas available, and temperature of the cooling water supply (8).

There are two trends quite noticeable in ammonia synthesis plant design at the present time. One of these is the design of large ammonia plants ranging in size from 600 to 1,200 tors per day capacity. These depend on the availability of an adequate supply of low-cost process material, usually natural gas, plus a large ammonia market close by, or the availability of low-cost water transportation. For example, liquid ammonia is now being shipped from South America to the United States and Europe in tank ships that can carry 9,000 tons of ammonia.

The design trend in these large plants is toward the use of centrifugal compressors for synthesis gas compression, and toward the use of operating pressures in the range of 150 to 200 atmospheres. The centrifugal compressors may be driven by gas turbines or by steam turbines, and their use results in a marked decrease in maintenance over the reciprocating compressors previously used, and a great decrease in the number of operating units required, which simplifies the piping and reduces the number of operating personnel required.

The second trend in ammonia plant design at present is towards the design and construction of relatively small anamonia plants that are prefabricated or "package" plants. These consist of a number of factory assembled

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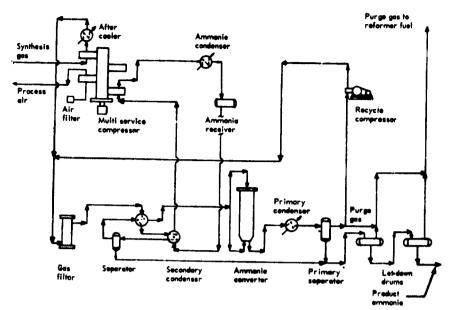


Figure III. Ammonia synthesis

units — compressors, catalyst vessels, gas purification units, control centres etc., that can be shipped to a plant site, connected together and placed in operation in a few weeks' time, as contrasted with the erection period of several months or a year required for a field erected ammonia plant. Typical examples of this type of plant are the sixty and one-hundred-ton-per-day AMMOPAC plants being built by Girdler Corporation. Figure IV shows a typical sixty-ton-per-day AMMOPAC installed in the State of Texas in the United States.

# VI. LARGE VERSUS SMALL AMMONIA PLANTS

The decision as to whether to build one very large ammonia plant as opposed to several smaller plants represents a very complex problem because of the extremely detailed marketing and transportation analysis that must be made for each individual venture. Figure V shows approximate battery limits ammonia plant investments based on prevailing United States Gulf Coast construction costs. Figure VI shows the cost of producing

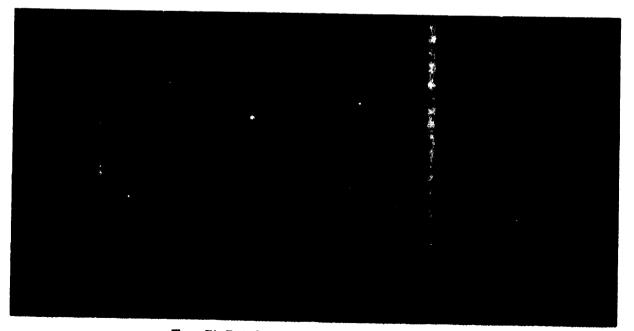


Figure IV. Typical sixty-ton-per-day AMMOPAC installation

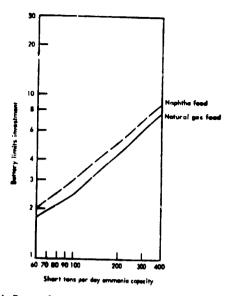


Figure V. Battery limits ammonia plant investments based on steamhydrocarbon reforming and electric motor compressor drives

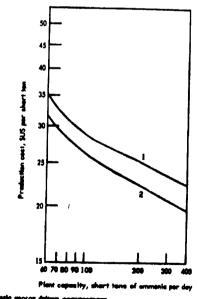
ammonia from various size plants based on today's cost of natural gas, electric power and general utilities in the same location. As stated before, an approximation can be made from these numbers for investment and manufacturing cost for the partial oxidation system, again on United States Gulf Coast basis. It should be noted that the investment figures given are for battery limits plants only and the addition of offsites could almost double those numbers for a complete grass roots facility.

At first glance, it would appear that the most economical approach to the manufacture of ammonia would be to build the one very large plant that would be required to supply the entire needs of a developing nation. The error in this conclusion is in the fact that cost of transportation has been neglected. Returning to the hypothetical case presented in the first part of this paper, if one 400 ton per day plant were built it would then be required to supply nitrogen fertilizers to all areas of that country; whereas, if four 100 ton-per-day AMMOPACs were strategically located throughout this country the average distance that the ammonia would have to be transported would be reduced considerably. In fact, in a country of even moderate geographical size this could easily amount to an average savings of 300 miles per ton of product shipped. Using the average railroad freight rates prevailing in the United States of America today, this would be the same as adding about \$11.00 per ton to the cost of the ammonia delivered from one 400-ton-per-day plant over that from four 100-ton-per-day plants. This, applied to a 400-ton-per-day ammonia production, could amount to about \$1,500,000 per year savings by strategic location of the smaller plants.

Another very important, but possibly more obscure advantage is the reduction in time required to get into production afforded by the AMMOPAC. Obviously, a 400-ton-per-day ammonia plant would have to be field erected as its physical dimensions would be much too

large to permit skid mounting. The field erection on such a plant outside the United States would require about twenty-two months up to the point where the plant would be producing ammonia. Whereas, the 100-tonper-day AMMOPAC, being almost entirely fabricated in a shop under controlled conditions of both weather and quality of workmanship, would require only thirteen months. Eight months of this would be procurement and fabrication in the shop, two months for shipping and no more than three months for final field erection. An example of this technique was recently covered by most of the technical magazines in the United States of America when the Girdler Corporation in Louisville, Kentucky loaded an entire prefabricated 60-ton-per-day AMMOPAC on one LST in Louisville, Kentucky, from whence it was shipped directly to France.

A third, and very important, advantage of entering the nitrogen fertilizer manufacturing business via the small unit is the fact that it allows a developing nation to enter this field with a much smaller initial investment by doing so in a step-wise fashion. One approach to this procedure would be to start out with one 100-tonper-day plant and, as the market developed and the economy improved, the additional capacity would be added one plant at a time until all four had been installed. As can be seen from figure VI, the cost difference between producing ammonia in a 400-ton plant as opposed to a 100-ton plant is roughly \$6.00 a ton, but it has previously been shown that a savings of \$11.00 a ton might be realized by the strategic location of smaller plants. In addition to this economy, the installation of the smaller plants would result in nine months additional production due to the shorter schedule. If the ammonia was sold at, say, \$92.00 a ton at the plant and the cost of manufacturing was \$26.00 a ton, the additional revenue in this



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Figure VI. Cost of producing anumonia in different size plants, based on US gulf coast conditions

ninc-month period generated by only one 100-ton-perday AMMOPAC would more than represent the total difference in investment between one 400-ton-per-day plant and all four of the ultimate 100-ton-per-day AMMOPACs. This additional production because of the nine months' difference in schedule -- could easily result in the addition of one complete growing season to the over-all cconomy of the developing nation and could substantially shorten the time required to generate sufficient capital to afford installation of the additional plants.

As noted before, it is impossible to generalize on an international basis so as to present economics adequate for detailed analysis of any given set of conditions existing in each of the various developing nations. However, during the course of the conference adequate time should be available for discussion of specific cases.

## VII. UTILIZATION AND DISTRIBUTION

The ammonia produced in a synthetic ammonia manufacturing plant is obtained as a high purity liquid, containing about 99.8 per cent ammonia and 0.2 per cent water. This product will either be used as it is, or converted to chemical derivatives such as nitric acid, ammonium nitrate, calcium ammonium nitrate, ammonium sulphate and urea.

The use of fertilizers is very seasonal, with the greatest usage taking place in a period of one or two months each year, generally in the early spring. Since ammonia must be produced at an even rate throughout the year to make effective use of the manufacturing plant, it is necessary to provide large-scale storage facilities for ammonia and its derivatives.

Liquid ammonia is somewhat lighter than water (its specific gravity is 0.62 at  $60^{\circ}$ F), and has a boiling point of  $-28^{\circ}$ F at atmospheric pressure. Consequently, it must be stored under pressure if kept at ambient temperature. The vapour pressure of liquid ammonia is approximately 200 pounds per square inch gauge pressure at 100°F. Ammonia is sometimes stored in uninsulated steel tanks with capacities up to about 100 tons each. This type of storage is used only to a limited extent, because of the large quantity of steel required for the pressure tanks. Ammonia is sometimes shipped in uninsulated steel tank cars, which contain about 26 tons each.

Some use is being made of insulated steel spherical storage tanks which contain about 2,000 or 3,000 tons of liquid ammonia, stored at a temperature of about 30°F and 45 pounds per square inch gauge pressure. The liquid ammonia is kept at this temperature by autorefrigeration, that is by allowing the liquid to boil, and then compressing and reliquefying the resulting vapour.

The principal method now being used for storing large quantities of liquid ammonia is to store the ammonia at atmospheric pressure in insulated steel tanks which contain the ammonia at  $-28^{\circ}$ F. The ammonia is maintained at this temperature by auto-refrigeration, with the ammonia vapour being continously recompressed, liquefied and returned to the storage tank. Single tanks have been built with a capacity as high as 30,000 tons. Such a tank might be 160ft in diameter and over 80ft high. While many of these large storage tanks are located adjacent to ammonia manufacturing plants, others are located at terminal points where liquid is supplied from barges or ships, and then is unloaded from the storage tanks either for sale or for use in adjacent plants making ammonia derivatives such as ammonium nitrate. Refrigerated ships are now hauling loads of as much as 9,000 tons of liquid ammonia from South America to both Europe and North America.

While ever-increasing amounts of ammonia are being used as fertilizer by the direct injection of liquid ammonia into the soil, the bulk of the ammonia is converted to other products before it is used as fertilizer. Nitric acid is a major component of nitrogen containing fertilizers. It is produced by the catalytic oxidation of ammonia with air, followed by absorption of nitrogen oxides in water to produce nitric acid. Nitric acid is a very reactive and corrosive material, and is ordinarily converted to other products at the time and place of manufacture, with only sufficient storage being used to provide operating flexibility.

Ammonium nitrate is produced by reacting nitric acid directly with ammonia. It is dried and sprayed to produce pellets or prills, which consist of pure anhydrous ammonium nitrate, and which are then coated with 2-3 per cent of an inorganic coating agent such as diatomaceous earth, and are bagged to give fertilizer grade ammonium nitrate, which contains 33.5 per cent nitrogen. This product is one of the main fertilizers made from ammonia.

Ammonium nitrate may be stored as the 83 per cent liquid product from the reaction of nitric acid and ammonia, and then converted to solid prills during the fertilizer sales season. In this case, it is stored in large tanks which may contain 10,000 tons or more of ammonium nitrate solution. In other cases, the animonium nitrate is converted to solid prills, bagged, and the bags are stored in warehouses until the fertilizer season arrives. Warehouses may store 10,000 to 20,000 tons or more.

Calcium annonium nitrate, containing 20.5 per cent nitrogen, or thereabouts, is produced by mixing limestone or dolomite with ammonium nitrate solution and prilling or granulating the product. It is a less concentrated source of nitrogen than ammonium nitrate, but is favoured in areas where the soils need the addition of lime as well as nitrogen.

Another major fertilizer product is urea, which is made by reacting ammonia with carbon dioxide. It is rapidly increasing in production because of its high nitrogen content (46 per cent) and its wide field of application (9).

The carbon dioxide required for urea is ordinarily supplied from carbon dioxide recovered as a by-product during the production of ammonia synthesis gas, so that urea manufacturing is usually carried on adjacent to ammonia production. Urea is produced as crystals, prills and as aqueous solutions. The prills may be stored in bulk in warehouses, or in bags. Storage facilities for 20,000 tons or more of urea are in use to provide inventories for use during the peak fertilizing season. Mixtures of ammonia, ammonium nitrate, urea and water in various combinations, are in common use as nitrogen solutions, containing specified percentages of fertilizer nitrogen ranging as high as 49 per cent N. These are in common use for direct application as fertilizers, and also are used for blending into mixed fertilizers to provide the required nitrogen content. These solutions may be kept in large storage tanks, and can be shipped in tank cars and tank trucks, so they represent a substantial outlet for ammonia in a form that can be readily stored shipped and used.

Ammonium sulphate produced by reacting ammonia with sulphuric acid, and then crystallizing and drying the product to produce a fertilizer containing 20.5 per cent N, has been a standard fertilizer for many years but is now being displaced by ammonium nitrate and urea. Ammonium sulphate production requires a supply of sulphur or sulphuric acid in addition to ammonia, and produces a fertilizer of relatively low nitrogen content, as contrasted with ammonium nitrate and urea, which have higher nitrogen contents and which are produced entirely from ammonia and ammonia by-products.

Sodium and potassium nitrates have been used for many years as nitrogen containing fertilizer materials, the principal source being the natural deposits of sodium nitrate in South America. Like ammonium sulphate, the relative importance of these products is declining, as compared with ammonium nitrate and urea.

Complex fertilizers, prepared by digesting phosphate rock with nitric, phosphoric or sulphuric acids, followed by ammoniation and blending with potash salts, are becoming an increasingly important outlet for ammonia and nitric acid, since both of these products are used in the manufacture of the complex fertilizers. These fertilizers are produced in a wide range of formulations with varying nitrogen contents, and may be stored in bulk in warehouses, so they provide a means of storing ammonia for peak fertilizer seasons.

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# 5. PROCESSES FOR PRODUCTION OF CONCENTRATED FERTILIZERS

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The NP and NPK fertilizers contain side by side nitrogen, phosphoric acid and potash, the most important nutrients for good plant growth. In the field of agriculture the use of NPK fertilizers brings about considerable labour savings as compared to the application of single fertilizers. The desire to likewise cut the cost for transportation and storage led to the development of the concentrated complete fertilizers, typical examples of which are the products NPK 15/15/15 and NP 20/20/0. 100 kg of NPK 15/15/15 are equivalent to the following quantities of single fertilizers:

71.5 kg sulfate of ammonia		15 kg N
75.0 kg superphosphate		15 kg PaOa
25.0 kg potassium chloride		1.4.1

i71.5 kg = lotal quantity

Today, concentrated complete fertilizers form an essential part of the fertilizer production in Europe and in the United States of America. It is quite obvious that the production of fertilizers should also be initiated as soon as possible in developing countries.

The following are the most important questions connected with the production of concentrated complete fertilizers:

(1) What formula should be chosen?

(2) What process should be chosen?

With reference to question: (a), a formula in which the proportional weight relation of N,  $P_aO_5$  and  $K_aO_5$ is 1: 1: 1 to approx. 1: 1: 0.5 will be in order for common agricultural cultures. Since nitrogen represents the most important plant food and as it should repeatedly be applied to the soil in always sufficient quantities, a single nitrogen fertilizer should be kept available for dunging the soil during vegetation besides the NPK fertilizer. Including these additional amounts of single nitrogen, phosphoric acid and potash will now be: 2: 1: 1.

This again means that 50 per cent of the total amount of nitrogen required should be produced and applied in the form of an NPK fertilizer and the remaining 50 per cent in the form of a single fertilizer. The above formulas and proportional relations of the nutritive substances are physiologically and statistically established values. Yet, for the chemical composition of the NPK fertilizers and for the choice of relevant manufacturing processes other considerations will have to be taken.

With reference to question (b), in principle, for the nitrogen component the choice is to be made between

sulfate of ammonia and ammonium nitrate. Sulfate of ammonia is less hydroscopic and its action somewhat slower than that of ammonium nitrate, yet, its use causes soils to consume larger amounts of calcium.

If sulfate of ammonia is applied permanently, the soils will become sour. A yearly amount of approximately, 100 to 200 kg CaO/ha (200 to 400 kg of calcium carbonate) will have to be added to the soil in order to make up for the CaO losses caused through the use of sulfate of ammonia. Sulfate of ammonia contains 75 per cent of sulfuric acid, which in turn means that in countries that do not dispose of sulfur deposits of their own, high expenditures for sulfur imports will become necessary.

Finally, mention must be made of the fact that the use of sulfate of ammonia having a nitrogen content of only 21 per cent is less rational than the application of e.g., ammonium nitrate containing 33 per cent N or urea containing 46 per cent N. Ammonium nitrate which in Europe is given preference to other nitrogen salts is produced exclusively from ammonia, which means that from ammonia also the nitric acid required for the production of ammonium nitrate is produced.

The increased hygroscopicity is disadvantageous for ammonium nitrate as compared to the less hygroscopic sulfate of ammonia. Yet, the hygroscopically more favourable behaviour of the sulfate of aminonia by no means implies that in tropical climates first class and possibly moistureproof packing of this salt — that is soluble in water — could be abandoned. In this connexion it is pointed out that fertilizers containing ammonium nitrate should best be packed in plastic bags. Hence, such bags made of polyethylene or PVC should be used in any developing country as packing material for nitrogen fertilizers.

The above comments on sulfate of ammonia and ammonium nitrate apply in the same form to the complete fertilizers which contain these substances. The complete fertilizers can be produced by either using nitric acid or sulfuric acid. When using sulfuric acid the less hygroscopic complete fertilizer of sulfate of ammonia and ammonium phosphate will be obtained, while when using nitric acid as in the Hoechst Process for the production of complete fertilizers, complete fertilizers containing ammonium nitrate with dicalcium phosphate and ammonium phosphate as components of the phosphoric acid will be obtained. The special features and characteristics of the above two processes are dealt with in the following sections. Here, the economic advantages of the Hoechst Process for the production of complete fertilizers on the basis of nitric acid deserve special attention.

# A. PROCESS USING SULFURIC ACID

Phosphoric acid is produced from rockphosphate and sulfuric acid. By neutralization of phosphoric acid or a mixture of phosphoric acid and sulfuric acid by means of ammonia, ammonium phosphates or mixtures of ammonium phosphate with sulfate of ammonia will be obtained.

Using customary granulating equipment the primarily produced salt suspensions are processed to granulated NP products. In this way formulas, such as NP 18/46, NP 19/19, NP 20/20 can be obtained.

The phosphoric acid contained in the neutral products is completely soluble in water. By adding potash salts in the granulating process various NPK products can be obtained.

In setting up the complete production plant, the following installations are required:

(a) Plant for the production of sulfuric acid.

(b) Plant for the production of phosphoric acid;

(c) Neutralization and granulating plant.

In the plant for the production of phosphoric acid approx. 400 to 450 tons of gypsum per 100 tons  $P_gO_g$ will be obtained as by-product. The entire amount of calcium in the rockphosphate is contained in this waste product, whose utilization (e.g., as gypsum for construction purposes) is difficult and whose removal may require high costs. The entire process is frequently used for the NP and NPK products although the consumption of sulfuric acid per 100 tons  $P_sO_g$  and 100 tons N amounts to approx. 600 tons  $H_sO_q$  in the NP product.

# B. Hoechst-Uhde PROCESS FOR THE PRODUCTION OF COMPLETE FERTILIZERS USING NITRIC ACID (SEE FIGURE)

In this process, rockphosphate is processed to concentrated NPK products and ammonium nitrate/limestone (ANL) by means of nitric acid and ammonia. Waste products are not obtained hereby. From rockphosphate and nitric acid a solution of phosphoric acid and calcium nitrate is first produced, from which by means of cooling

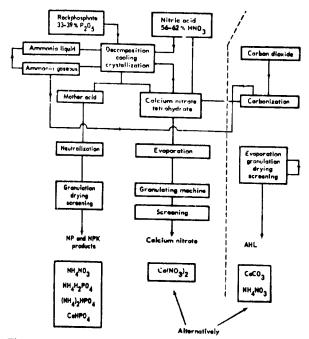


Figure 1. Flowsheet — Hoechst process for the production of complete fertilizer

and crystallization 50 to 70 per cent of calcium nitrate is removed and separated in crystalline form.

The mother acid strongly enriched by phosphoric acid is neutralized with ammonia and further processed to NP and NPK products in customarily used granulating equipment. Hereby such products as NP 17/24, NP 20/20 and the well-known NPK products as e.g., NPK 15/15/15 are obtained.

The calcium nitrate obtained in the process can be evaporated directly to the calcium nitrate fertilizer. Yet, of great advantage is the processing of the salt to ANL which is achieved by using ammonia and carbon dioxide (from the ammonia production).

While in process A above per 100 parts  $P_8O_6$  — as e.g., in NP 20/20 — only 100 parts of nitrogen are produced,

-
\$11 Mio
500 tons NP 20/20
450 tons CAN 21 per cent N
None
150 tons line extracted from restphosphote and to yield CAN
None
No loss if CAN is applied to- gether with NP-product

with the Hoechst Process for the production of concentrated complete fertilizers up to 190 parts by weight of nitrogen are obtained per 100 parts of  $P_sO_s$ ; 100 parts N in the product NP 20/20 and 90 parts N in the form of the single fertilizer ANL.

In carrying out the process, the following installations are required:

(a) Plant for the production of nitric acid;

(b) Plant for the production of complete fertilizers with granulating plant;

(c) ANL production plant with granulating plant.

The investment costs as calculated on the  $P_sO_s$  capacity are somewhat higher for the Hoechst Process than for process A. Yet, in return, the amounts of nutritive substances and fertilizers produced are essentially higher. It is of great importance that when using the Hoechst Process no sulfuric acid will be required and that no waste products will be obtained.

The dica/cium phosphate which besides phosphate of ammonia is contained in the NP products causes the fertilizers produced not to be completely soluble in water. The efficiency and nutritive effect of the  $P_gO_g$  for plants is not impaired thereby. Numerous tests and the favour-

able results achieved in the practical application give proof of the high quality of the products. In Europe again and again new plants are being set up although the present capacity has already reached 4 million tons per year, i.e., approximately 500,000 tons  $P_sO_s$  per year. A comparative study of the figures for processes A and B shows the advantages of process B.

### CONCLUSIONS

The Hoschst Process for the production of complete fertilizers as described under section B is economically superior to process A working with sulfuric acid. The products obtained in process A deprive agricultural soils of considerable amounts of calcium. The products obtained in process B have the same effect on the growth of cultivated plants as the products obtained in process A.

In setting up a fertilizer industry in developing countries processes A and B are appropriate. In either process concentrated, easily transportable and highly efficient NP and NPK fertilizers are obtained.

By using process B, the entire demand of agriculture for concentrated complete fertilizers and single nitrogen fertilizers can be covered.

# 6. PLANT SIZE, LOCATION AND TIME-PHASING The nitrogenous fertilizer industry

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## 1. SUMMARY

This is the sixth in a series of studies dealing with plant size, location and time-phasing. Two reports have concentrated on mathematical model building. This marks the fourth application of the model to specific Indian industries: caustic soda, cement, aluminium, and nitrogenous fertilizers.

The report outlines the basic data adopted for the nitrogenous fertilizer industry — the choice of products, processes, capital and operating costs, transport costs, and state-wide estimates of demand. The following are the principal conclusions:

(a) It would be economical to standardize ammonia plants at a single size for single-stream units: 200 thousand tons per year. With the plant size restricted to this one level, the gains from standardization appear to outweigh the costs.

(b) There are economic advantages in concentrating fertilizer production in 200-thousand-ton units located at regional petroleum refining centres, and transporting products to the markets in individual states. If, however, there are compelling political reasons to take up the production of fertilizer on a state-by-state basis, then there are significant benefits derived from time-phasing the projects so that two adjacent states do not construct plants simultaneously.

(c) Unlike the previous results for caustic soda, coment and aluminium, where the present licensing policies result in plant sizes that appear unduly small, the official programme for new plants in the fertilizer industry generally corresponds to the sizes indicated by our analysis.

(d) There is a heavy reliance upon the North-West refinery (assumed location — Rajasthan) for maphtha. This assumption needs continuing scrutiny if the nitrogenous fertilizer industry is to meet its output targets.

(e) The "representative points" adopted for each state have not been chosen with sufficient care to insure minimization of *intre-state* transport costs of final fertiliners. In order to select the exact plant locations and in order to plan the supply of negleths from the nearest refinery, it would be essential to calculate these points more accurately.

## 11. DEMAND FORECASTS

In the Perspective Planning Division (1964), it has been estimated that a nitrogen fertilizer equivalent of 1.75 million tons will be demanded in 1970-71. This will be the target adopted here, even though other sources have estimated it at higher levels.

Our best estimate of actual consumption in 1965-66 works out to the equivalent of 0.75 million tons of nitrogen. Of this, 0.50 million tons are expected to come from domestic output, and the rest will be imported. (This is the same ratio between domestic output and imports that prevailed during 1962-63. See Fertilizer Association of India (1963).) By 1970-71, we assume that the utilization rate of capacity will be improved sufficiently so that this source of additional capacity will be just sufficient to handle the domestic consumption being satisfied by imports during 1965-66. Thus the total output from new plants to be constructed during the Fourth Five-Year Plan is 1.00 million tons of nitrogen.

Based on the fertilizer dose recommendations tor various crops in different states and earmarking certain areas to be fertilized, state-by-state forecasts are made in table 1. The area to be fertilized under each crop is determined on the basis of present levels and trends of fertilizer consumption over the past years as well as the magnitude of the over-all fertilizer target. Due account has been taken of the priority of irrigated and rain-fed areas to be covered by the fertilizer programme. The fertilizer requirements for plantation crops have been allocated to states, for example, all tea has been put under Assem. Coffee has been apportioned between Kerala and Madras in the ratio 1: 2, and rubber is assigned entirely to Kerala.

III. CHOICE OF SOLID FERTILIZERS AND PRODUCT-MEX

There are a variety of solid nitrogeness fertilizers which deserve consideration depending on soil conditions, water logging in cropped fields and the case with which the fertilizer can be applied. A judicious choice of the specific products to be produced in a State will depend on the erop structure and agrenomic conditions. The fertilizer recommendations of the Fertilizer Association

## TABLE 1 PROJECTED BEAMOR FOR NETERISATION FEBTULINES BY STATES (All Approx in risowand matrix tage)

		-			
	/960-da	<b>1979-7</b> 1	722	Antibad Marinadar	
South-Barr	390.6	494.1	1130	22 78	20 72
Andhra Pradauh	195.8	227 3	71 5	14.30	18.65
Madras	134.8	177 2	42.4	1.46	11.07
South-West.	82.9	/9/ 7	100.8	21 76	
Nêyapre	4.1	120.0	75.8		<b>39</b> .99
Kernin	38.7	71.7	13.0	15.16 6.60	19.70
See.		-	-		8.61
	70.7	19 <b>6.8</b>	126.1	25.22	建 🖤
Astan West Bones	36.0	61.0	25.8	5.16	6.73
Origen	24.0	<b>89.0</b>	65.0	13. <b>#</b>	16.96
	10.7	46.8	35.3	7 <b>•</b> 1	9.21
North-East	126.2	378.8	252.6	10.52	65.91
Dihar	42.4	£13.8	71.4	14.38	16.63
Utter Predesh, Best	50.3	i 59.0	HOB. 7	21 74	20.37
Utter Predesh, West	33.5	196.0	72.5	14.50	10.91
North-West	<b>40</b> .0	223.0	135.0	H.M	<b></b>
Penjab, Jamma and Kashmir	<b>97</b> 2	197.0	99.1	19.96	25.49
Rejection	10.8	46.0	95.2	11.04	14.40
West-Central	53.7				
Guineat		154.3	<b>100</b> u	<b>10</b> .12	36,39
Madbys Produch	<b>26.4</b> 27.3	<b>84.</b> i	<b>97</b> 7	11. <b>50</b>	15.00
		78.2	48.9	8.50	£1.39
Adabarashira.	37.9	200.9	143.0	30.60	37 <b>30</b>
Mahurashte	<b>97.9</b>	200.9	545.0	38.60	<b>77.30</b>
Toras, ali india.	798.0	1,750.0	1,000.0	300.00	200.00

 Based on mix of 1.6 tens uses and 1.5 tens summanism valphate per ten of enteriods. Mitreagen contexts of these products are 46 per cent and 21 per cent, resulting in 8.77 tens alleragen per ten of enteriods

of India provide the dose in terms of astrogen and the approximate time at which application is feasible — oropwise — is each State but acthing about the type of fortiliner. Ammonium sulphate is the most widely used fortilizer we various soils and orops. The whole of this product is water soluble, has good storage qualities and is easy to handle. Uses contains 44-46 per cent of nitregen per ten. It is likely to be backed out from the seil and should not be applied to acids containing free wells is product is a problem oven if it is evaluable in pelled form. Uses could, however, is conplayed in merihern areas for orops requiring less water, or where kherif and rabi orops are grown under controlled artigotion.

There are specific uses in which it is advantageous to utilize other forms of nitrogeneous fortilizer, announced ablevide, ammonium aitente, anneutrien exiptate-aitente, attransmum phosphote, and aqueous annexes. Here that ammonis is an intermediate in producting each of these products, and that the value added is the conversion presses is lower than the cost of the measurables. Some, for purposes of advantag an optimal assurables, phose day, it essented best to study a duple min of finalized products. As a min that might be appropriate under ladies conditions during the Pourth Plan, we have chosen accession subplace and ures. Accession subplace is a welltonally popular factilizer. However, per ten of attrages, area is less expensive to produce, and also has the advantage of heing the least bulky solid product. Whenever transpert costs are proportional to bulk, this persuite supplying silvages at the lowest transport cost to the consumer. Ures is also therefore a product which is forecassible to large plant sizes for amsteals.

There are 0.00 tests of assessmin required per tes of area and 0.26 tests per tes of assessmin relation. Our typical mix is expressed in terms of the approximat assessmin is terms of the approximat assessmin resulting in 1 test of true and 1.5 tests of relations as end products in the assessment of additional functions.

# IV PERSON SPACE OF THE INDUSTRY

Table 3 indicates the location of onising and proposed facilities factories in India as of July 34, 566. The appalty ranges up to 360 thereased metric tags per year of strongen. Hangel, the largest plant in 1666, is based on electrolysis of water and has the highest costs. Several of the existing facilities plants are working well below capmoity typically for lack of raw materials or electricity rather than lack of domand.

We cannot be seriain of the enset quantity of dispatches for the mitial conditions of our model as of 1965-46 It is assumed, however that with better capacity utiliasnom the 1963 level of imports could be virtually wiped out.<sup>1</sup> As can be usen from the table, a variaty of netrogeneous fertilizers are being produced and plasmed ammonium sulphate, ammonium sulphate-seriete, urea, caloium ammonium-netrate, etc. As of 1963, the factures incested in Bibar. Orizen, Madhya Pradech, and some in Uttar Pradech were operating on ocal, and only a small quantity of output was based on neglethe-based process since as will be seen later, it is less expensive than cool.

<sup>1</sup> Otherway we would have to allow for continuous imports of at least 250,000 tons, or would have to provide additional expansity in the Pourth Plus to establish this basibleg of internal domaind.

# V RAW MATERIAL AVAILABILITY

For ammonia manufacture, the choapest raw material available in natural gas " Natural gas has been found in Naharhatiya in Assam, and explorations are progressing in Rajasthan and Punjab. We did not study this aspect in detail since the Assam region has a low demand for fortihaer and could be supplied either through natural gas or through the surplus naphtha available there.<sup>3</sup>

Many of the existing plants are coal-based, but the cost and availability of ecoal as specified in Indian Statistical Institute (1963) suggests that there is hardly any justification for coal-based fortilizer plants except in Bihar and Madhya Pradesh. Even in these regions, as will be seen below, other cost factors are unfavourable to coal.

<sup>4</sup> Other raw massrials such as onke oven gas or refinery gas are by-products available from other processes and could conservably be chauper in some situations. These are neglected here

\* A small plant based on natural gas is likely to go shortly into production in Assam.

r I

Table 3. LOBARTON OF MARKE REVEALED FORTHARD PACTURES AS OF JULY 31, 1963 -

A contraction		Capavity.
	Product	mattike sana Bati sanar
		d atteagan
In geodystem		
1. Sindri, Bilter	Ammonium oxigitate	75,300
3. Always, Rosala	Amenorium edgilane	28,999
3. Mindel, Miller	Antennium subplicite-advate	36,489
4. Bouchelo, Orizzo	Cubine antioutum-aligne	
5. Hangel, Paujab	Cultures annouture-alterate	8,400
•• • •		
kinneni ani sut to go into pradastipo		
6. Hannap, Aman	Ammonium sulphate	23,600
7 Admente, Marala	Annovius mighate	38,950
8. Hannangarb, Bajashan	Anomenium mighate	N.,100
R. Beurluin, Chings	Cubitors annonium-albudo	
H. Betlageden, Anders Product	Line .	
H. Manurap, Antonio		86,479
18. Barreth, Cedarar	View	26,200
18. Wayneld, Mindrage	time.	4,00
	Una .	71,100
14. Treasley, Madazastara	Line .	-
16. Geneldigen, Ulter Product	Voe	
14. Burgapus, West Rangel	Urap .	
Planant and put to be Recently		
M. Mangalana, Mpanpa		
18. Martin, Manfigo Pradoch		30,000
M. Mangalana, Mynamo		

· Street, Partition Association (1988).

and and the set of the

··· Plannand tons per year )

		Maxer	evallabilies of explicitu	Hor -suptor aptric and operachemicals	Nor craitain for clice and
I	Koyali Ballasry, Experts	1966-67	620	241	179
		1978-71	140	442	230
2	Marth West Ballnury Rupathan*	1970-71	488	148	292
÷	Cashin Ballnery Korala	1966-67	175	87	
		1978-71	173	H	365
4.	Bombay Robornes, Maharashtra	1985-67	961	102	687
		1978-71	992	403	100
\$	Madras Bolinery, Madras <sup>10</sup>	1976-71	480	387	195
6	Visse Rolinery Andhra Pradoch	1965-67	186		144
		1978-71	346	99	205
7	Assum and Bihar Belinerias	1966-67	740	122	446
		1978-71	732	172	440
8.	Makin Ballnery West Dangel	1978-71	997	350	1 97
•	Polgi	1970-71	4,590	1,445	2.147

\* Extently to units on stream in 1969

Literby to some on stream in 1967

Librity to come on stream in 1968

4 The Perspective Planning Division (1966) provides for 1.8 million term of naphths for familiant in 1978-71 and 2.8 million tone in 1975-76

Naphtha (boiling paint 158-350°F) is obtained as a joint product in the fractional distillation of crude oil. It is used primarily as a component of motor spirit Therefore, the availability of naphtha will depend on the domand for motor spirit, and the regional patterns of ris availability can readily be altored by a change in gasoline blonding and distribution practices Table 3 groome annually and another scalability of nephthe after making allowance for motor spirit and petrochemieals. Note that in seven of the eight refinery areas, there would be enough surplus naparita evailable to serve as foodstook for a 280-thousand-tons-por-year ammonia plant

## VI. CHERCE OF PROCEES. UAPITAL AND OPERATING CERTS, SCHOOLSHED-OF-SCALL

Here we discuss the cost of angliths versus coal as internative row materials for sumonia production. Natural gas steam reforming is less capital-intensive, but the reasons for not considering it have already been indicated in the section on raw material avail iliter. The costs of annucain production are likely to be 50 per cost or more of the total costs in a fartilizer plant, and it is therefor eccential to select a minimum-next process for this \_sermediate. The following are estimates of cepital costs for a 100-thousand-ton-per-your automin t based on three alternative processes and row muterial combinations:

Magdala		referring 4	54.00	(11)	<b>Ba.</b> )
History	 partial s	e-dilition	 (7.3)	-	Ba.)
Cast		entidative			

\* This is the latest small " This is the inter predictly presses. For a detailed ( of the presses and costs, one J. Vaugel and J. Televany (i

The costs for the steam-reforming process in India are obtained by inflating United States costs of crosted plants by 40 per cent, as suggested in an unpublished petro-chemicals report by the French Petroleum Institute. The other estimates are from Indian project records

When a ton of naphtha is assumed to cost Rs. 35 and coal (10,000 BTU/16.) Is valued at Rs. 23 per ton, operating ones (proportional to output) per tos of ammonia by the above processes are respectively Rs. 166.48, J04.76, and 213.58 blove details are given in tables 4 and 5. The cost structure there suggests that it is con-siderably changer to adopt the naphtha-steam reforming -----

Ammonia is made by combining nitrogen and hydro-gen. (The corbon dioxide evaluable as a by-product in the manufacture of ammonia is sufficient to convert the entire ammonia into urea by the total recycle process.) Witrogen is obtained from air either by distilin tion of liquid air or by romoval of eaugen through a combustion tes. The main east saving can be seen through the following chemical reactions

Steam reforming:	Nydrumrben + stumm + sir + hydrugen	+
Perilal emidation	allengen + earben mononids hydroenrisen + engens + steam > hydrogen earben menonidis	+

<sup>1</sup> Under de mentes service continues provides is lede, de res of metebols is provide provide to fair de restance de families is provide provide to fair de restance de families interest of a subset provide to a subset of a service continues of a subset provide to a subset of a service continues of a subset provide to a subset of a service continues of a subset provide provide to the service continues of a subset of a subset of a service continues of a subset of a subset of a service of a long dimension has able of and has been been broad a long dimension has able of and has been been broad a long dimension has able of and has been a broad a long dimension has able of a long broad broa

· her : battet dennten of protection and f and her b

The steam reforming process results in a mixture of hydrogen and nitrogen which can be combined in a 3. I ratio to produce ammunia. The partial oxidation process requires a separate liquid air discillation unit as a source of nitrogen. Until recently, partial oxidation has been in vogue because of its flaxibility. This process makes it presible to shift from one raw material to another in the same plant. But, after the most recent developments in the steam reforming process for asphtha, the partial enidation process source definitely disadvantageous. For these reasons, our plant size analysis is confined to the steam reforming process.

information on investment costs was available for United States created plants of various sizes for the steam reforming of asphiba.' The range of sizes covered is

<sup>2</sup> This information was very bindly provided to us by Mr. Taki Rifler of the Prench Perceloum Institute. from 50,000 tons to 200,000 tons per year of ammonia, and are all on the basis of single-stream plants. Within this range, the scaling factor is 0.79.\*

On the basis of the available investment costs for urea and ammonium sulphate plants," the scaling factor for an integrated naphtha-based nitrogenous fertilizer complex is taken to be 0.73. Using this scaling factor together with the investment costs for the standard size plant shown in table 5, we have extrapolated to obtain the investment costs at all other levels of capacity. One qualification: for ammonia plants beyond 200,000 tons per year in capacity, it is believed that the incremental

\* The scaling factor varies from 0.63 for coal-partial exidation (the most capital intensive) to 0.88 for steam reforming-natural gas (the least capital intensive).

\* These are available in the United Nations (1963), and show good agreement with Indian project reports.

## TABLE 4. OPERATING COM PROPARTIONAL TO OUTPUT ( Re. per los of animonia)

		Magala		Mayrial anti	no-angratige Allow	Cost-pareta/ ontification	
• · · · · · · · · · · · · · · · · · · ·	········	<b>Ø</b> 19.	Cuu	<b>.</b>	Cast	<b>e</b> w	6.999
Naphtha	85/1en	0.885	78.13	6.825	70.13	-	
	35/tun 6.66/21/1/b	720	43.20	1.400	17.00	2.65	47 15
	15 and 8.4/ton			2	38.60	1,9 <b>30</b> 4	115.00
Presses water	0.25/10 <sup>2</sup> gal.	75	18.75		1.67		33. <b>60</b> 1.67
hiller find water	1.00/10 <sup>p</sup> gal.	1.40	1.0	.36	.36	.36	
Chambab and supplies.			12.00				
Labour and supervision .	•	-	15.00	-	15.00		15.00
Tens. (Ba./ten)			108.46		204.76		213.50

Brenetto: Per steam referring process - J. Veepi and J. Tistreey (1963). For other processes - Indian project separts.

	···· (K.)-···			Antyskowi Antyskowi Antyskowi	r and by		
	- <u>.</u>	<b>8</b> w.	Garr	<b>Øw</b> .	Cirr		Case
	100-10/tup *		16.20			0.26	41.72
	Million		-	6.36	64.75		
	The fight of the second					4.80	68.12
		200	15.00		3.00		1.0
		<b>5.</b>	1.37	1.5	6.30	4.5	1.13
hiter had water	Langer and	_		6.27	6.17		
	-		100			-	
Labour and experiation			8.00	-			16.00
Tornes (Ba./han)		-	101.05		3.0		107.37

## (In. per im of product)

Circuit : Indigo grains gauge

" Calles desite all is militie in a set for mouth day.

" Happening and an and brand has done onto

## TABLE 5. INVESTMENT COSTS OF STANDARD SIZE PLANTS ( Rs. millions present worth,

discounting in perpetuity at 10 per cent per annum)

		Ammonia : ngghalu : stoam : refer ndng :	Ammonia coal-parisal cridation)	Urea- ammonium vulphare including ammonia from naphtho- steam reforming i
	Size (10* come ye )	100 ammenia	100 ammania	100 uroa 130 miphate
1.	Initial investment once for all time	J4.00	<b>92</b> .93	109.12
2.	Replacement of initial in- vestment every 24 years *	5.40	9.29	10.91
3.	Maintenance and overheads 6 *, of item (3) per year in perpetuity.	32.40	\$5.76	65.50
4.	Total present value (10 <sup>4</sup> Rs )	91. <b>8</b> 0	1.57.96	185.53
Ec	conomiss-of-scale parameter.	.79	.63	.73

SOURCES: For steam reforming process --- J. Voogd and J. Tietrooy (1963). For other processes --- Indian project reports.

investment costs would continue to decline. In order to err on the conservative side, we have assumed that the incremental investment costs for these large plants will remain constant at the same level as estimated for a 200,000-ton plant.

## VII. FURTHER COMPARISON OF INVESTMENT COSTS FOR COAL WITTING NAPHTHA PROCESSES

In terms of operating costs, we have already noted that naphtha has an advantage of Rs. 54 per ton of ammonia is against coal (Rs. 160 wraw 214). In this section we compare the ammonia investment costs associated with these two raw materials, taking due account of the differences in economies-of-scale. The costs of future installations are calculated using a continuously compounded discount rate of 10 per cent per year. Capacity costs are based upon those shown in table 5 for a single standard installation; i.e., they already include an allowance for the installation, replacement every twenty-feur years, and maintenance and overheads rs 6 per cent per year on the initial investment. For plant  $si_{700}$  other than the standard ones shown in table 5, an economies-of-scale factor of 0.79 is applied for naphtha-based plants and one of 0.63 for coal.

The capacity costs shown hereafter refer to the series of future installations required in order to satisfy the constantly growing demand over an infinite horizon. With a discount rate of 10 per cent and scaling factors of 0.79 and 0.63, the optimal cycle times are 4.5 and 8.5 years respectively between successive ammonia installations in a single region. (See figure 1 in Report Number 1.) Table 6 expresses the investment costs in two ways: (a) the present value of the rupees expended over an infinite horizon, using the optimal cycle time between installations (see eq. 1.2 in Report Number 1), and (b) the equivalent cost of this capacity per ton of future demand and output (see eq. 3.2 in Report Number 3).

Table 6 makes comparisons of investment costs assuming that after 1965-60 each of the fifteen states will be self-sufficient with respect to increases in ammonia demand.<sup>10</sup> Even with this decentralized pattern of production, it is clear that naphtha-bused plants would be less expensive than coal. The investment cost saving ranges from Rs. 64/ton of ammonia in Uttar Pradesh, East up to Rs. 110 in Madhya Pradesh. These amounts, when combined with the operating-cost saving of Rs. 54/ton, would far outweigh the cost of transporting naphtha into the coal-producing states that have no refineries. Hereafter, our analysis assumes that all new nitrogenous fertilizer plants will be based upon naphtha.

### VIII. TRANSPORT COSTS

In order to proceed with the evaluation of alternatives, we now introduce estimates of transport costs. The rates shown in table 7 are applicable to rail shipments by wagon loads. To these are added a 5 per cent surcharge to arrive at the actual rates charged during 1964. The rail distances between representative points were shown previously.<sup>11</sup>

In the caustic soda report (Number 2 within this series) appendix B referred to the controversy over the telescoping pattern of the tariff structure (the increment in rate per unit increment in distance). It appears inappropriate to review this controversy again here.

Just as excessive telescoping leads to a bias in favour of a small number of large plants located at long distances from their markets, so also does a rate structure that artificially permits the shipment of finished fertilizers (urea and ammonium sulphate) at much lower rates per ton of bulk than for the raw materials, nephtha and ammonia (see table 7). For want of a better alternative, we shall assume that the 1964 rate structure is a rational

<sup>&</sup>lt;sup>4</sup> With a plant life of trenty-four years and a 10 per cent per year discount rate, the replacement factor turns out so be 10 per cent of the institual investment. (See eq. (2.1) of Report 1. Number 2 in this series.) From the viewpoint of a private investor, this tweaty-four years service tife for a fertilizer plant would almost surely be regarded as excessive. The private investor would base his calculations upon a shorter service life, e.g., ten years. With a ten-year service life and a 10 per cent discount rate, the replacement factor would these his calculations upon a shorter service life, e.g., ten years. With a ten-year service life and a 10 per cent discount rate, the replacement factor would the be raised from 10 per cent of the initial investment. This would have the direct effect of raising the calculated cost of producing fertilizer. It would, however, have the initial custlays for plant investment rather than upon the current outlays for transportation. That is, a lower service life would have than is indicated below in table 8.

<sup>&</sup>lt;sup>10</sup> Note that Utter Predezh is divided into two parts, with Kanpur as the representative point in the Bast and Delhi in the West. The Jammu and Kashmir domands are consolidated with those of the Punjob. Negaland, Manipur and Digure domands are consoldreted with those of Access.

<sup>&</sup>lt;sup>14</sup> Table 1, Report Mumber 1 in this Series, see page 1.

	Annual Increase In demand ( thensand	Optimal ; i thencend te	Plant size Na per year)	gresent <b>mfm</b> ite	ent costs, value over horizan illions) *	investme equivalent of future and ou	demand
	year of annunumia)	Naphtho- based	Cont- based	Naphthe- hased	Casi- based	Naphtha- based	Coal- based
South-East					·		4 - Marine - Ar Angel
Andhra Pradesh	18.7	85					
Madras.	11.1	50		<b>222.8</b> 146.5		119	
South West				140.3		132	
Mysore	19.8	90	170	233.1	107 (		
Kerale	8.6	40	170	122.8	387.6	118	196
Rest				144.0		143	
	6.7	30		97.9			
West Bangal	17.0	80		212.4		146	
Orises	9.2	42		127.7		120	
North-East				147.7		139	
Dihar	18.6	85		222.8			
Utter Predech, East	28.3	128	244	306.5	489.3	119	
Utter Predech, West	18.9	LS .	163	222.8	378.3	109	173
North-West					378.3	118	200
Punjab, Jamme and							
Kashmir	26.0	117	224	206.0	462.2		
Rejestien	14.4	65		180.3	484.2	110	178
West Cantral				1.44		125	
Gujarat	15.1	6		186.8		124	
Madhya Pradesh	11.2	50	96	146.5	270.6	124 132	343
Maharashira				. 40.3	2/V.U	134	242
Maharashtra	37.3	168		361.7		103	

TABLE 6. INVESTMENT COST COMPARISONS BETWEEN COAL AND NAPHTHA PROCESSES FOR AMMONIA; SINGLE-PHARE CYCLES; DECOUNTING AT 10 PER CENT PER YEAR

· Equation 1.2 in Report Number 1 in this perios.

\* Reportion 3.2 in Report Number 3 in this series.

one based upon the long-run marginal railway costs. This assumption is exceedingly dubious. It is quite likely that the rail rates discriminate unduly against the transport of "dangerous petroleum products". The discriminatory aspect of the rate structure will surely come under closer scrutiny at a future time when India begins to plan pipelines for the transport of refined petroleum products as well as for prude oil.

Before examining the combined effect of transport costs and economies of scale in manufacturing, there is one alternative which will be noted briefly and then disearded: the possibility of partial integration between ammonia and fertiliner plants. That is, because of the weight-gaining mature of the process of converting onia into fertibizer, it is sometimes desirable to earry on the two stops at two separate locations. In the present case, there are several reasons which led us to omit this possibility. These reasons might well be re-examined if one were to make a more detailed study of the industry:

(a) The instanton of uses in the product-main devours an roted plant. Otherwise, the cost of a uses plant potterns of time-phasing and location. The loca žd bo jes

rate plant for the manufacture of carbon dioxide --- which is available as a free by-product in ammonia production.

(b) It costs more to transport naphtha in the intermediate form of ammonia than in the form of naphtha as such. This will be illustrated at a typical interstate distance: 500 kilometres from a fertilizer plant to its source of naphtha at the nearest refinery. According to table 7, at this distance the transport cost of these alternatives would be as follows;

Naphtha as such	<b>Rs. 65.60</b>
Naphtha in the form of ammonia:	per ton asphthe
1 ton ammonia Rs. 71.40	Ra. \$6.50
.825 tone nephthe × ton ammonia	per ion asphile.

## IX. COST COMPARISONS, SINGLE-PHASE AND TWO-PHASE CYCLES

Table 8 summarizes the costs of three altern mand by the necessity of setting up a cope- patterns are based upon a grouping of the states int

TABLE 7. RAILWAY FREIGHT RATES, WAGON LOADS

		Rs. per meir	ic ron of bulk	
Kilometres	Nap <b>hika</b>	4mminia	.4mmontum sulphare	Urea* (for agricul ural use only)
1-70	14.10	15.30	6.00	7. <b>2</b> 0
71-150	23.70	25.70	9.10	11.00
151-200	29.30	31.80	10.70	12.90
<b>201-250</b>	34.80	37.80	12.20	14.80
<b>251-</b> 300	40.10	43.60	13.60	16.50
<b>301-</b> 350	45.30	49.40	15.00	18.30
<b>351- 400</b>	<b>\$0.6</b> 0	<b>55.1</b> 0	16.40	20.00
<b>401- 450</b>	55.90	60.90	17.90	21.80
<b>451- 500</b>	61.00	66.40	19.20	23.40
<b>501- 550</b>	65.60	71.40	20.30	24.80
551- 600 · · ·	70. <b>30</b>	76.60	21.50	26.30
<b>601- 650</b>	75.10	81.90	22.70	27.80
651-700	79.9 <b>0</b>	87.00	23.90	29.20
701-750	84.70	92.30	25.10	30.70
751-800	89.40	97.50	26.40	32.20
801-850	93. <b>40</b>	101.80	27.40	33.40
851- 900	97.30	106.00	28.40	34.70
901-950	101.10	110.20	29.30	35.90
951-1,000	105.00	114.40	3 <b>0.3</b> 0	37.10
<b>,001-1,100</b>	112.50	122.70	32.30	39.60
,101-1,200	120.20	131.10	34.30	42.00
<b>,201-1,300</b>	127.80	139.40	36.30	44.40
, <b>301-1,400</b>	134.90	147.00	38.00	46.50
<b>,401-1,500</b>	141.90	154.70	39. <b>70</b>	48.60
<b>,501-1,600</b>	148.80	162.30	41.40	50.70
,601-1,700	155.90	170.00	43.10	52.80
<b>,701-1,800</b>	162.80	177.50	44.80	54.90
<b>,801-1,900</b>	169.90	185.20	46.50	57.00
,901-2,000	175.70	191.60	48.00	58 80
, <b>001-2,10</b> 0	180.00	196.20	49.10	60.20
,101 <b>-2,2</b> 00	185.30	202.00	50.60	62.00
<b>,201-2,300</b>	190.50	207.80	52.00	63.80
,301 and above	193. <b>20</b>	210.60	52.70	64.60

SOURCE: Indian Railway Conference Association, Goods Tariff No. 31A, part II, Goods Rate Tables in force from 1.7.1962.

\* This rate is admissible only when the urea is certified "for agricultural use" by the Ministry of Food.

seven regions — each with a regional centre containing an oil refinery. In all cases, the cycle time is held constant at 6.0 years' worth of growth in demand, an interval which is optimal for single-phase cycles with a discount rate of 10 per cent and an economies-of-scale parameter of .73 for the ammonia, urea and ammonium sulphate complex. The three alternate cases are distinguished as follows:

Case A. Single-phase cycles: each state perpetually supplies itself; plant size = 6.0 years' worth of demand growth in individual state.

Case B. Single-phase cycles: each regional centre perpetually supplies all states in its region; plant size = 6.0 years' worth of demand growth in region.

Case C. Two-phase cycles: regional centre alternates in capacity construction with other states in the region; plant size = 6.0 years' worth of demand growth in an individual state. In table 8, the discounted costs are broken down into three components: manufacturing costs subject to economies-of-scale, transport costs for the naphtha feedstock, and transport costs for the finished fertilizer. Details on computing the manufacturing and product transport costs have already been indicated. (Equations (1.4), (1.5), and (2.3), Reports Number 1 and 2 of this series.) Annex A below contains similar details on the naphtha raw material transport costs.

Among the three patterns of time-phasing and location shown in table 8, note that case A always minimizes the cost of transporting the fertilizer product to the consuming market; that case B minimizes both the costs of manufacturing and also the costs of transporting naphtha; and that case C is an intermediate one in each cost component. Of the three cases, the total discounted costs are minimum for case B (Rs. 6,131 millions), and slightly more for case C (Rs. 6,205 millions). The total discounted costs for case A (Rs. 6,851 millions) work out to be approximately 10 per cent higher than for either case B or C.

The policy of locating large plants at regional centres (case B) is desirable not only on the basis of the cost calculations presented in table 8, but also because this policy facilitates the standardization of plane sizes in all regions at 200 thousand tons per year of ammonia (see below). If, however, there are compelling political reasons to take up the production of fertilizer on a state-by-state basis, then there are significant benefits from time-phasing as shown in case C. In case C, both the sizes and locations of plants are identical with those of case A. These two differ with respect to time-phasing. Case A possesses an advantage in only one of the three cost components: costs of transporting the final product to the second area to meet its growth in demand during the first phase of each cycle. This minor advantage in fertilizer transport costs is more than offset through: (a) the usual reduction in manufacturing costs from postponing the date of the capacity investment in the second area and (b) the saving on transport of naphtha feedstock during the first phase whenever the first area contains an oil refinery and the second does not.

One additional calculation was made concerning plants designed to serve individual state market areas. This case was similar to case C: two-phase cycles, regional centre alternating with other states in its region. Instead of the uniform cycle time of 6.0 years employed in Case C, each region's cycle time was set so as to be consistent with the construction of 200-thousand-ton ammonia plants within one of the states included in that region. (Within the other states of the region, non-standard size plants were to be built at the appropriate phase of each cycle.) This pattern of size, location, and time-phasing made it possible to reduce total costs to Rs. 6,061 millions. With this policy, however, standardization of plant sizes throughout India becomes difficult to achieve.

## X. COSTS OF PLANT SIZE STANDARDIZATION

Up to this point, we have neglected the costs and benefits of standardizing the sizes of new fertilizer plants. By standardization, we mean identical single-stream units 

 TABLE 8. Cost comparison for alternative patterns of plant location and time-phasing; cycle time of 6.0 years \*

 (All figures in Rs. millions of costs discounted at 10 per cent per year)

R	South-east	South-west	East-west	North- East	North-west	West- central	Mahu- rashtra,	<u> </u>	
Region	Madras,	Kerala,	Bengal,	Bihar,	Rajasthan,	Gujarat,	Maha- rashira None	Total all India	
Other sta	Andhra Pradesh	Mysore	Assam Orissa	Uttar Pradzsh, East and West	Punjab, Jammu and Kashmir	Madhya Pr <b>a</b> desh			
Case A	Manufacturing costs b.	753	722	894	1,505	936	691		
Single-phase:	Naphtha transport •	0	87	45	226	180	68	744	6,245
each slate perpetu-	Fertilizer transport	0	0	0	0	0	0	0	606
ally supplies itself	TOTAL, CASE A	753	809	939	1,731	1,116	759	744	0 6,851
Case B				· · · · · · · · · · · · · · · · · · ·					-
Single-phase :	Manufacturing costs b.	631	606	682	1,158	786	579	744	
regional centre per-	Naphtha transport *	0	0	0	0	0	0	744 0	5,186
petually supplies all	Fertilizer transport	141	128	109	320	177	70	Ő	0 945
states in its region	TOTAL, CASE B	772	734	791	1,478	963	649	744	6,131
Case C									
Two-phase :	Manufacturing costs <sup>b</sup> Naphtha transport <sup>c</sup>	664 0	644 84	766	1,343	826	601	744	5,388
regional centre	Fertilizer transport	7	4	41 9	219	169	61	0	574
alternates with other					9	7	7	0	43
states in its region	TOTAL, CASE C	671	732	816	1,571	1,002	669	744	6,205

 End products are urea and ammonium sulphate in product tonnage proportions of 1:1.5.

Includes only those manufacturing costs subject to economies-ofscale. Does not include those costs proportional to output and summarized in table 48: Rs. 122.66 per ton of ures and Rs. 127.37 per ton of ammonium sulphate.  Naphtha transport costs calculated on assumption that Mysore would receive naphtha from Madras; Orissa from West Bengal; Madhya Pradesh from Gujarat; Punjab from Rajasthan; Uttar Pradesh, East from Bihar; and Uttar Pradesh. West from Rajasthan.

- specifically excluding multiple-stream systems of equivalent capacity. The benefits to be derived from standardization may be listed as follows:

(a) Savings in capital costs by ordering several identical units at the same time or by ordering duplicate units even if ordered at different times;

(b) Savings in spare parts inventory;

(c) Facilitates transfer of operating experience from one fertilizer plant to another;

(d) Facilitates the domestic manufacture of equipment.

With these benefits in view, we studied the effect upon costs if plants were restricted to a single standard size: 200 thousand tons per year of ammonia in single-stream plants.<sup>18</sup> To simplify the problems of plant location, timephasing and product-mix, the benchmark conditions are taken to be those of case B, table 8: single-phase sixyear cycles, naphtha converted into a mix of urea and ammonium sulphate, and each regional centre perpetually supplying all states in its region.

According to table 9, standardization would entail negligible departures from the cost minimum calculated for the non-standard plants appropriate for each region. The only significant discrepancy occurs within the north-east region, a cost increase of 1.5 per cent. If table 9 is at all representative, it is clear that the benefits

TABLE 9. COST COMPARISONS BETWEEN STANDARD AND NON-STANDARD PLANT SIZES, SINGLE-PHASE CYCLES; EACH REGION PERPETUALLY SUPPLIES ITSELF

								Present value of a (Rs. millions discounsed	nanufacturing custs   at 10 per cent per year)
								Costs based on non-standard plants, table 8, case B	Costs based on standardised 200-theneand-sen plants for each region
South-east .								631	631
South-west .								606	609
East								682	682
North-east .	•							1,158	1.175
North-west.	•	•						786	787
West-central								579	579
Maharashtra	•	•	•	•	•	•	•	744	744
			τ	01	AL			5,186	5.207

 Includes only these manufacturing costs subject to economics of scale within a complex whose and products are una and assumation millions.

<sup>&</sup>lt;sup>18</sup> With an on-stream officiency factor of 330 days per year, this size corresponds to 600 tons of ammonia per stream day. This is a popular size for plants currently under construction in the United States of America.

outweigh the costs of standardization, and that the 200-thousand-ton plant size is a reasonable standard for India. This size coincides with current official thinking for units to be initiated during the Fourth Plan. These units are considerably larger than those licensed and yet to go into production as of 1963 (see table 2 above).

## X1. COSTS PER TON OF NITROGEN

For comparison with cost figures cited in other sources,<sup>18</sup> it may be of interest to summarize the results of the model into a single figure: Rs. 714, the equivalent cost per ton of nitrogen demanded and produced. In arriving at this total, we will first convert the results of case B, table 8 into the corresponding unit cost. This figure includes all manufacturing costs subject to economies-of-scale plus the cost of transporting naphtha and fertilizers. It excludes the proportional manufacturing costs shown in table 4 above, and also excludes the costs of distributing fertilizer to the farmer from a plant located at the representative point of each state:

Ex-factory cost per ton of ni- trogen demand and produc- tion; excludes proportional manufacturing costs	Discounted costs case B, table 8	Rs. 6,131 millions			
	Discounted tons of nitrogen de- manded and produced; *	0.2 million tons/(.10) <sup>a</sup>			
	= Rs. 307 per t nitrogen	on			

\* Equation 3.2 in Report Number 3 in this series (see page 1).

In table 10, the proportional operating costs per ton of bulk product are converted into the costs per ton of nitrogen, assuming that a representative mix would consist of urea and ammonium sulphate. With the proportional costs at Rs. 407, the total ex-factory costs become Rs. 714 per ton of nitrogen = 307 + 407.

#### Annex A

#### RAW MATERIAL TRANSPORT COSTS IN TWO-PHASE CYCLES •

Consider two areas 1 and 2, where the first area has a naphtha surplus and the second a deficit in this raw material. Suppose that a fertilizer plant is constructed in area 1 at the beginning of the first phase of each cycle, and one is built in area 2 at the beginning of the second phase. There is a penalty for transport of the finished product from area 1 to 2 during the first phase.<sup>b</sup>

We now have to evolve an expression for the transport of raw material to area 2. It will be convenient to use the following symbols:

- $D_j = Annual increment in demand in area j (j = 1,2)$
- t Time interval between successive plants in a given area
- $t^{\bullet} = tD_1/(D_1 + D_2)$

T = Any arbitrary point in time

- r = Annual discount rate, compounded continuously
- c = Cost of raw material transport per unit of output of end product

• This problem also arose in connection with Report Number 3, "The Cament Industry". No details were given there on the manner of calculating transport costs for the raw material, coal.

 $^{\bullet}$  This penalty function  $F(r,t^{\bullet})$  is tabulated in table 2, Report Number 1 of this series.

If it were not for the temporary saving on transport of naphtha into area 2 during the first phase of each cycle, we could write the discounted costs of raw material transport over the infinite horizon as follows:

Discounted costs, excluding 
$$m = c \int_{0}^{\infty} \tau D_{\mathbf{y}} e^{-t\tau} d\tau = \frac{c D_{\mathbf{y}}}{r^{3}}$$

During the first phase of each cycle until time t<sup>\*</sup>, there is a temporary saving in naphtha transport. Summing these savings over all future cycles of length *t*:

Discounted value of 
$$\frac{c \int \tau D_3 e^{-r\tau} d\tau}{1 - e^{-r\tau}} = \frac{c D_3 [F(r, t^*)]}{1 - e^{-r\tau}}$$

Combining terms, we have the desired result:

Discounted costs of raw material transport = 
$$cD_3 \left[ \frac{1}{r^4} - \frac{F(r, t^*)}{1 - e^{-rt}} \right]$$

TABLE	10.	OPER/	TIN	G CO	its p	ROPORTIONAL	TO	OUTPUT;
PR	ODUC	T-MEX	OF	URBA	AND	AMMONIUM	SUL	HATE

	Product tota par tot of anomonie	2 ous nitrogan		Operating costs propertional to output		
		Per son of product	Per ion of animatic	Per sea of product from sable 43	Per ten of annualis	Per sen of nivegan
Ures	1.0	0.46	0.46	Rs. 123	Rs. 123	
Ammonium sulphste	1.5	0.21	0.31	127	190	
TOTAL	2.5 tops		0.77 tons		Rs. 313	Rs. 407

<sup>&</sup>lt;sup>18</sup> E.g., in Perspective Planning Division (1964), table B3 indicates the ex-factory price of nitrogenous fertilizers as Rs. 1,200 per metric ton of nitrogen. Note that this price is set so as to cover costs of production under unfavourable circumstances: random interruptions due to shortages of raw materials and power, obsolete processes based upon raw materials other than naphtha, and small plants.

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# 7. RECENT TRENDS IN THE AMMONIA INDUSTRY IN JAPAN

Shinhiro Kodama, Sumitomo Chemical Company, Itd., Japan

1. THE HISTORY OF THE NITROGEN INDUSTRY IN JAPAN

Japan, Europe and North America are the three areas in the world where the nitrogen industry has been highly developed. We will discuss the history of the development and the status quo of the nitrogen industry in Japan. We will touch on some of the problems the Japanese nitrogen industry is now facing and will also try to give some suggestions to the representatives of countries which are now planning or have started to develop a nitrogen industry.

Japan is known for her high density of population and scarce natural resources. Consequently, Japanese agriculture was destined to become an intensive cultivation. This situation gave impetus to farmers to use fertilizer, and encouraged industrialists to produce it in large quantity at low price; thus, the nitrogen industry was developed at a rapid speed. Table 1 shows the present position of Japanese nitrogen industry in the world. The ammonia synthesis process which was industrialized by BASF in 1913 was imported in to Japan shortly after the First World War and in 1923 the Casale process of Italy was introduced and employed at Nobeoka Plant of Nippon Chisso or the Japan Nitrogen Fertilizer Co.

After that, until shortly before the Second World War the Japanese nitrogen industry developed smoothly, as indicated in table 2. A considerable number of plants had been constructed, and by 1940 there were as many as twenty (seventeen companies), while production capacity reached 1,900,000 tons in ammonium sulphate equivalent.

One of the factors which contributed to this rapid development was the government's protection of the nitrogen industry by means of financial support as well as by a preferential tax system.

The Second World War had, however, adversely affected the industry and bombing dealt it deadly blow. In 1945 the production capacity of ammonium sulphate had fallen to 180,000 tons.

When the war was over, people faced a disastrous food shortage and it became of paramount importance for the Government to increase the output of rice and grains.

Pure necessity drove the government as well as industrialists to the quickest possible rehabilitation of the nitrogen industry. The Government took emergency measures to reconstruct the industry, such as preferential loan or the preferential allocation of materials. As the result of this policy coupled with the strenuous effort of industrialists, the Japanese nitrogen industry recovered rapidly, as shown in table 3 and figure I, and by 1950 the production capacity had reached 1,860,000 tons in terms of ammonium sulphate, which means a 100 per cent revival of the capacity of pre-war days.

During this period, however, the industry laid primary emphasis on the increase of production, without due consideration of cost reduction, consequently the plants reconstructed were almost exact reproductions of the pre-war plants and no tangible technical innovation was seen. For example, as shown in table 3, from 1945 to 1955 the raw materials for hydrogen had hardly been changed. From around 1950, however, the circumstances changed gradually, and the industry was forced to change the direction of its effort toward cost reduction. Such changes have been brought about primarily for the following reasons :

(a) The rapid expansion of production resulted in an over-supply and the surplus products had to find their outlet in overseas markets where they had to compete with European products.

(b) This has demanded the reduction of production cost. One of the principal efforts of the Government was to stabilize the price of rice, which has been the main expense of the people, and for that it was necessary to supply fertilizers at lower price.

Under these circumstances, the modernisation of the nitrogen industry had been positively promoted with some financial assistance of the Government. In the first period (1953-1958) \$214,000,000 was disbursed for plant modernization and in the second period (1959-1962) \$189,000,000 (total \$403,000,000) was invested.

Out of these sums, 40-50 per cent was invested for ammonia plants, while the rest was directed to the production of urea and compound fertilizers, etc.

On the other hand, during the progress of such modernization, there occurred some notable changes, such as:

(a) Petroleum became cheaper than coal, as hydrogen source;

(b) New technology such as the Texaco high pressure gasification process was developed.

The situation in this period is illustrated in tables 3 and 4. In 1953, 26.4 per cent of the hydrogen for the nitrogen industry was supplied by electrolysis of water, while 68.5 per cent was produced from coke or coal. However, in 1963 the percentage of ammonia produced by water electrolysis and coal gasification decreased to 5.2 per cent and 6.8 per cent respectively. Instead of these, hydrocarbon oils, natural gas and residual gas from petroleum refining have come to be utilized and ammonia from these raw materials reached to 42.4 per cent, 20.8 per cent and 8.4 per cent of total production, respectively. The output of ammonia which is produced from coke oven gas has increased from 5.1 per cent to 15.4 per cent during 1953-63.

As is evident from the above, during the ten years after 1953, the Japanese nitrogen industry switched over its raw materials from coke and coal to petroleum, natural gas, coal gas and the residual gas from refinery or petrochemical plants.

The details of this transformation are given in table 4 with a break-down by year and the names of companies.

Table 4 also indicates what processes have been employed in such a conversion to petrochemical materials. The process most popularly used was the Texaco's crude oil gasification, which is utilised under 30 kg/cm<sup>2</sup> of pressure.

For converting natural gas into raw gas for ammonia synthesis, they employed Grande Paroisse's process which uses normal or 7 kg/cm<sup>a</sup> of pressure or the CCC process of 7 kg/cm<sup>a</sup> or 11 kg/cm<sup>a</sup> as well as the Fauser process of 15 kg/cm<sup>a</sup> of pressure.

Others employed the normal pressure crude oil gasification process of the Fauser or of the Sumitomo Chemical Company or Shell's crude oil thermal gasification under 30 kg/cm<sup>2</sup>.

11. RECENT PROGRESS OF INDUSTRIAL AMMONIA SYNTHESIS, AND FUTURE PROBLEMS OF THE JAPANESE NITROGEN INDUSTRY

### A. General outline

The Japanese nitrogen industry completed its modernization programme by 1962 and the hydrogen source was changed from coal to petroleum. Although only two years have passed since the completion of the programme, it has already been superseded by the most advanced technology. During these two years, quite a number of new ammonia synthesis methods have appeared. Hereunder is given a brief explanation of some of the most interesting new processes.

As is well known, the process of ammonia synthesis consists of the following five steps:

### (a) Gasification of raw material

Conversion of raw material, such as coal, gaseous or liquid hydro-carbons into  $OO + H_0$ 

### (b) CO-ahift conversion

Conversion of CO into hydrogen by the reaction :  $CO + H_0 = CO_h + H_h$ 

- (c) Removal of CO<sub>n</sub>
- (d) Removal of CO
- By these four steps, the minime of hydrogen and nitragen is produced from coal or petroleum, with a purity high enough for NH, synthesis.

(e) Ammonia synthesis

This mixture is finally converted into NHa.

# B. Some of the new processes

(a) Gasification

### (i) Steam reforming

These days it is more profitable to use natural gas or petroleum as raw materials for  $NH_3$  synthesis except in a few rare cases. There is a steam reforming process whereby these raw materials are reformed by the reaction with steam on a catalyst bed.

In this case, the reaction is an endothermic one as follows:

$$C_mH_n + mH_sO = mCO + \left(m + \frac{n}{2}\right)H_s$$

The required energy is supplied by the combustion of fuel outside the reaction tube.

### (ii) Partial oxidation

Partial oxidation process is the one where such energy is directly supplied to the reaction system, by carrying out the exothermic reaction simultaneously.

$$C_{m}H_{n} + \frac{m}{2}O_{n} = mCO + \frac{n}{2}H_{n}$$

In this case, air can be used as oxygen source to the extent that the final composition of the gas becomes  $N_1 + 3H_2$ . However, if it is with air only, the nitrogen content in the last composition becomes too high, and it is by all means necessary to use oxygen.

It is a recent tendency that in both of these cases, the process is used under pressure. This is because it can save the power required to compress the gas, as a considerable increase of gas volume takes place at the stage of gasification.

The Texaco process which is widely used in Japan, is a partial oxidation process without the use of a catalyst. Crude oil can be used as raw material in this process.

On the other hand, the Grande Paroisse Process is the partial oxidation process which uses a catalyst. By the use of a catalyst, it is possible to improve material consumption and utilities but it cannot treat crude oil, but only gaseous hydrocarbons or at best light naphtha. At present, the world supply of light naphtha is somewhat in excess; consequently, the ammonia synthesis starting from light naphtha is becoming popular.

Topsze-SBA autothermal process appeared recently as one of the catalytic partial oxidation processes. It is operated under 300-400 psig pressure to treat the light hydrocarbon feedstocks from methane to light naphtha. One of the advantages of this process is claimed to be the use of only one reactor.

Steam reforming processes have long been widely used for the manufacture of synthesis gas from natural gas. The one which is highlighted now is ICI's sterm-naphth reforming process. It is reported that ICI is already producing more than 2,000 t/d of NH<sub>0</sub> by this process. The advantage of this process is that it can use inexpensive naphtha as raw material and does not require expensive oxygen. But the question, of which is more profitable, partial oxidation or steam reforming, is dependent upon local conditions such as the cost of fuel or oxygen.

On the other hand, Topsæe, C.C.C., GP., GEGI., Zimmer, etc., are developing similar steam-reforming processes.

### (b) CO-shift conversion

A substantial quantity of carbon monoxide is always present in the gas obtained by gasification, although it varies according to each gasification process. For the conversion of carbon monoxide into hydrogen and carbon dioxide by the reaction with steam, Fe-Cr catalyst was used from former days. However, in this process, the reaction temperature was generally 350-500°C, so that the residual content of carbon monoxide in the gas was 2-4 per cent. The most remarkable development in shift conversion is the use of ZnO-Cr<sub>2</sub>O<sub>2</sub>-Cu catalyst developed by Girdler and CCI, where the reaction temperature has been lowered to 150-300°C and as a result it has become possible to reduce the residual content of carbon monoxide down to 0.1-0.5 per cent.

# (c) Removal of CO,

Carbon dioxide formed in gasification and CO-shift conversion must also be removed. In the conventional process it is removed by washing the gas under the pressure of 15-25 kg/cm<sup>8</sup>. Later, alkaline solutions such as Alkanolamine had come to be used. But recently the United States Bureau of Mines has invented the so-called hot-carbonate process, in which carbon dioxide is absorbed by 20-40 per cent of potassium carbonate solution at the temperature of 100-110°C and at the same temperature the absorbent is regenerated. The energy consumption has been reduced considerably in this process.

A process which has come to the fore recently is the Giammarco Vetrocoke Process. In this process carbon dioxide is absorbed at 60-65°C and the residual content of  $CO_3$  is reduced to 0.15 per cent, by addition of  $As_3O_3$  to the  $K_3CO_3$  solution, which accelerates both the absorption and desorption of carbon dioxide.

### (d) Removal of CO

Carbon monoxide should be removed to the order of several ppm, because it is a strong poison for the ammonia synthesis catalyst. In the past, to remove CO, the gas was washed with cuprous ammonia solution under 100-300 atm. However, this process requires considerable investment for the plant as it uses the expensive absorber and regenerating columns. But the operation cost of the plant is not low.

The process of washing the gas with liquid nitrogen has also been used but the cost of construction and operation is none the less expensive.

The method of removing carbon monoxide by converting it into methane through the following reaction has also been practised, but it had to be carried out at the pressure of 100 kg/cm<sup>8</sup>.

As already stated, in the conventional process of COshift conversion, 2-4 µer cent carbon monoxide remained, usually in the converted gas. Consequently, it was necessary to repeat CO-shift conversion and CO<sub>3</sub> removal a few times in order to decrease CO content to the level low enough to subject it to the methanation process. Therefore, it was not a favourable method for  $NH_3$ synthesis.

Recently, however, as mentioned before, due to the development of the catalyst for low temperature CO-shift conversion, the quantity of residual carbon monoxide can easily be reduced to 0.3 per cent. Thus it has become possible to remove CO by methanation at the pressure of 10-40 kg/cm<sup>2</sup> and to purify the gas to the extent that the total content of CO, CO<sub>2</sub> and O<sub>2</sub> becomes 10 ppm.

As a result of the development of this process, the cost of CO removal is expected to be lowered considerably.

### (e) Ammonia synthesis

 $N_3 + 3H_3 = 2NH_3$ 

It is well known that for the industrial ammonia synthesis the above reaction must be carried out under elevated pressure due to the equilibrium relationship.

In the Haber Bosch process, the first process for ammonium synthesis, this was carried out at 200 kg/cm<sup>2</sup>. The Claude process and the Mont Cenis process which were developed later used the pressures 1.000 kg/cm<sup>2</sup> and 100 kg/cm<sup>2</sup>, respectively. Recently, however, it

ESTIMATED COST COMPARISON BETWEEN A CONVENTIONAL PROCESS AND A NEW PROCESS South: 309 metric ton/day

NH, process	Paris	dde caat	Pin	M cour	Total 
e e and e e and e and e	<b>NT</b>	Percentage	\$/T	Personage	<b>(\$/T NH</b> _)
Creds oil high pressure partial exi-	27.70	65.3	14.72	34.7	42.59
High pressure steam naphtics refer-	27.50	76.5	9.44	36.5	36.94

seems that the synthesis pressure is settling down to ca. 300 kg/cm<sup>2</sup>.

For a synthesis catalyst, Fe containing small amounts of  $K_{2}O$  and  $Al_{2}O_{3}$  is customarily used. In this catalyst bed, there exists an optimum temperature distribution. Therefore the most efficient production of ammonia on an industrial scale can be realized by designing the reactor so as to maintain such temperature distribution, but it is difficult to maintain it at ideal condition because the reaction of ammonia synthesis is an exothermic one.

In the past, it was customary that the cooling tubes run inside the catalyst bed and the inlet gas cool down the catalyst while passing through the tubes. Later, Fauser invented a new method to cool the catalyst bed step-wise by hot water and, at the same time, to record at the reaction heat in the form of steam. According to the Kellogg method, the fresh gas is introduced into catalyst beds step-wise to control the temperature in the catalyst bed. Theoretically speaking, Fauser's steam recovery process is most advantageous. Recently, however, a process to use the pressure of 150 kg/cm<sup>4</sup> is said to be on the way to be developed to minimize power consumption by use of rotary compressors.

# C. Future problems of Japanese nitrogen industry

Although the modernization programme of the Japanese nitrogen industry was completed in 1962, further improvement of processes has already become an imminent need. There are a number of processes which may find their place in future attempts at improvement but among them the following processes are attracting particular attention.

(a) The newly developed steam reforming process and partial oxidation process, particularly the process to use light naphtha as raw material;

(b) The process which combines CO-shift conversion using low temperature catalyst and the methanation process for CO removal;

### TABLE I. ACTUAL PRODUCTION AND CONSUMPTION OF NITROGEN (1962-1963, fortilizer year) (Unit: 1.080 nitrogen Lon)

	Production	Communication		Production	Commente
Western Europe			North America		
Austria.	185				
Belgium	10) 300	<b>66</b>	Canada	471	149
Denmark		130	United States	4,152	4.420
France	_	147			
Poderal Rep. of Cormany	916	815	Sub-totai	4.623	4.560
Nely	1,467	1,005	Central America		.,
Notherlands.	\$20	471	Manine		
Norway	482	316	Others	65	175
Shelp	322	61		51	172
Spein	156	345			
Sweden Elmined Minachann	63	139	South America	116	347
United Kingdom	180	686			
Others	690	349	Chile.	170	26
			Ciliare	32	187
astorn Europe	5,581	4,583			· · · · ·
			Sub-total	222	213
Bulgaria a service a service a service a	105	125	Asia		
Carchesiovabia	161	195	China (mainland)	444	3.00
Restora Gormany	377	200	Indenseis		700
Bungary	75	110	India.	212	110
Poland	315	310	Jupon	1.201	400
	1.309	1.170	North Karen	-	819
Yugaslevis	25	120	Rep. of Kores.	<b>90</b>	100
	Ĩ	30	Publisten .		305
		-	China (Taiwan)		<b>90</b>
Sub-trant	2.484	2,300	Othere	70	135
New		4,000		51	486
United Arab Bass.					
	135	265	Granda	2,194	3,864
Seven Alter	115	110			
	•	126	Bulo-tatui	37	•

Boundary Minington, British Bulghur Corp. No. 37, 13 (1964).

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1945	46 (24.0)	49 (26.8)	90 (27-3)	<b>40</b> (21.8)	139 (76,0)	•	()	•		٠	0	39 (76.0)	183
	192 (20-7)		83 (14.2)	(11-7)	389 (70.31				0		0	399	511
4497	)48 (32.8)	<b>46:</b> (38.7)	300 (16.3)	120 (11.0)	74) (68.6)	•			•	٠	۲	(78-1) 741	1,009
448	478 (35.9)	<b>196</b> (3 <b>6</b> 1)	<b>380</b> (151)	: <b>10</b> (11-3)	855 (64.5)	•	٠					855	)   1,325
***	938 (38.3)	774 : (34.0)	<b>384</b> (17.3)	170 (10.3)	F.(186 (62.5)			85	٠	•	85	(64.5) 1,113	i,644
989	616	<b>62</b> 1 (33.3)	190 (17 7)	194 (10.4)	1,144	. ()	•	(5. <b>2)</b> 194	٠	•	(5.2) 104	(677) 1, <b>248</b>	1.864
991	<b>796</b> (38.1)	(35-3) (35-1)	486	205	(01.4) 1,006	•	•	( <b>5.6)</b> 111	•		( <b>5.5</b> )	(67.0) 1.554	2 796
982	790	499	(177) (199	(10.3) 200	(66.0) 1,750	•	•	(4. <b>8)</b> 136	٠		(4.8) 136	(67.9) 1.894	2.652
-	(28.5) 766	(37.7) : 1.110	( <b>10.6)</b> 971	(9.8) 300	(06.2) 1,900 -		•	(5.1) 147	•	•	(5.1) 147	(/1.4) 2,129	
<b>154</b>	(215.4) 700	(38.4) 1,100	(19.7) 688	(10.4) 300	(68.9) 3,698			( <b>5</b> .1) 1 <b>97</b>		6.7	(51)	(73.6)	2,892
	(25.3) 770	( <b>30</b> -3) 1 <b>,290</b>	( <b>30</b> . i ) 610	(8.9) 300	(00 3) 2,177	•	•	(5.2) 197		(0.2)	163 (5.4)	<b>2,26</b> 1 (74.7)	3,028
	(26.8) 814	(40), 9) 1,305	(19.9) 986	(9.4) 460	(10.7)	113	•	(5.9)	0	6.7 (0.2)	163 (5.2)	2,340 (75.2)	3,110
197	(38.7) 888	(30.7) 1,468	(15.7)	(13.0) 346	(85.9) 3,504	(8.1)	-	304 (7.0)	•	9.3 (0.3)	376 (10.4)	2,700 (77 3)	3,606
<b>4</b> 8	(19.3) 728	(34.3) 1,992	(13.6) 976	(12.0)	( <b>1</b> ).7)	365 (7.9)	174 (4. <b>8)</b>	300 (0.9)	۲	21 (0.5)	901 (21.0)	3,455 (80.7)	<b>4,28</b> 3
	(15.9)	(39.0)	(12.6)	480 (10.9)	2,487 (97-4)	348 (7.3)	204 (5.6)	<b>501</b> (10.9)	113 ( <b>1</b> .5)	10 (0.2)	1, <b>221</b> (26.7)	3,847 (84.1)	4,575
•	(12.0)	1,300 (36.9)	971 (10.0)	908 (9.3)	1,400 (46.0)	645 (12.0)	7 <b>90</b> (13. <b>9</b> )	996 (16.3)	<b>205</b> (4.7)	<del>))</del> (1.1)	2,239 (41.6)	4,707 (87.4)	5,300
	<b>67</b> (11.6)	<b>(14.2)</b>	972 (38.3)	<b>324</b> (5.3)	1,700 (31.0)	3,308 (26,0)	890 (±5.9)	996 (10.1)	384 (5.3)	<b>61</b> (7.1)	3,140 (57.2)	4,928 (89.0)	5,527
	<b>501</b> (0.7)	<b>(11)</b> († 1. <b>1)</b>	401 (7.3)	300 (6.3)	1,485 (38.9)	1,860 (90.9)	1, <b>190</b> ( <b>19.9)</b>	976 (9.4)	3 <del>1</del> 9 (5.4)	61 (1.0)	4,001	5,407	5,990
12	<b>609</b> (7.1)	177 (6.9)	485 (7.9)	<b>380</b> (0.2)	016 (13.0)	1, 788 (97.8)	i,300 (19.0)	071 (14.))	483	61 (1.0)	4,900	5,746 (92.9)	6,185
	300 (5.2)	•	486 (6.8)			3,548 (48.4)	1,485	1,006 (15.4)	573 (8.4)	71 (1. <b>9</b> )	6,885 (10.0)	6,490 (94.8)	6,845

FARES CHANNE OF ACTUAL NOR, FRIENDERCHINE CAPACITY (IN FINNE OF AND ONCH SULFATE) BROKEN BOWN ACCORDING TO HYDROGEN SOURCE (Unit 1,000 T/Y in terms of announcember)

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(e) The presses of one partitionies up en up to enterente qualizato fron the it of utili is of waste hand.

The following table shows the an m d i predenting overlaged pressure, tableg stancespilles the industry is one of these called "install-tion models of the standard pressure, tableg stancespilles the industry is one of these called "install-tion industries". The dense is industry is one of these called "install-tion industries". The dense is industry is one of these called "install-tion industries". The dense is industry is one of these called "install-tion industries". The dense is industry is one of these called "install-tion industries". The dense is industry is one of these called "install-tion industries". The dense is industry is one of these called "install-industries calculated". The dense of ensure and is down a categories is of the called "install-industries". The dense is industry is one of these called "install-industries". The dense is industries is one of the called "install-industries". The dense is industries is one is a standard with the is a capacity of 1,000 tens of assessing per day is one unit. The total reduction cost of Hill, by the ensure

III. Photo.com in the LAPLEM OF THE MIDDLEN MOLINEY

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onpacty of Jupanese nitrogen industry is 6,350,600 tensyear is ammonium suffate equivalent while the number of plants amounts to as many as twenty-seven. One of the deadvantages of the Jupanese nitrogen industry is therefore its insufficient unit capacity. This is rested in historical reasons connected with the development of Jupanese economy. It is advisable for a country which is trying to start its nitrogen industry to pay due consideration to the unit capacity so that this will not become too small. For this purpose it may be necessary to work out some programme for an international-job division.

### **B** Raw material

As regards the raw material for the nitrogen industry, encopt in cases where coal is particularly cheap, it is more profitable to use natural gas or potroloum hydrocarbons.

In a region where natural gas is obtained at low cost, it goes without saying that the utilization of natural gas in more economical. Where there is surplus of colle oven gas or residual gas from refinery, it is again natural to utilize them.

Particularly during the initial stages in the development of a petrochomical industry, the reasonal gas obtained from naphtha oracling for oldin production is most fitted to the synthesis of ammonia. From this viewpoint, it is profitable to construct petrochomical plants and ammonia synthesis plants on adjacent sites he part of one integrated project.

Whether orude oil or light naphtha is proforable as a source of hydrocarbons, is a matter dependent upon the case of procurement and the price at which they are obtained. If there is not much difference in price, it is by far more prolitable to use light naphtha, in view of the onse of processing and yield.

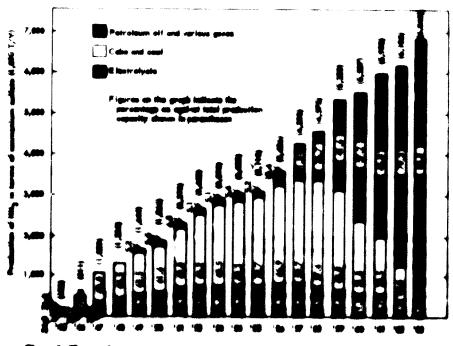
### C. Technology

<sup>p</sup>rom the economical standpoint we have to choose the most advanced technology. However such a problem as the choice between steam reforming and partial onidation is a matter depending upon relative factors in the places where low-cost electricity is available it is more profitable to use partial onidation, while at the stea where fact is chapter, it is the other way around. Therefore, the selection of the process should be done carefully based upon the industrial environment of each loughty.

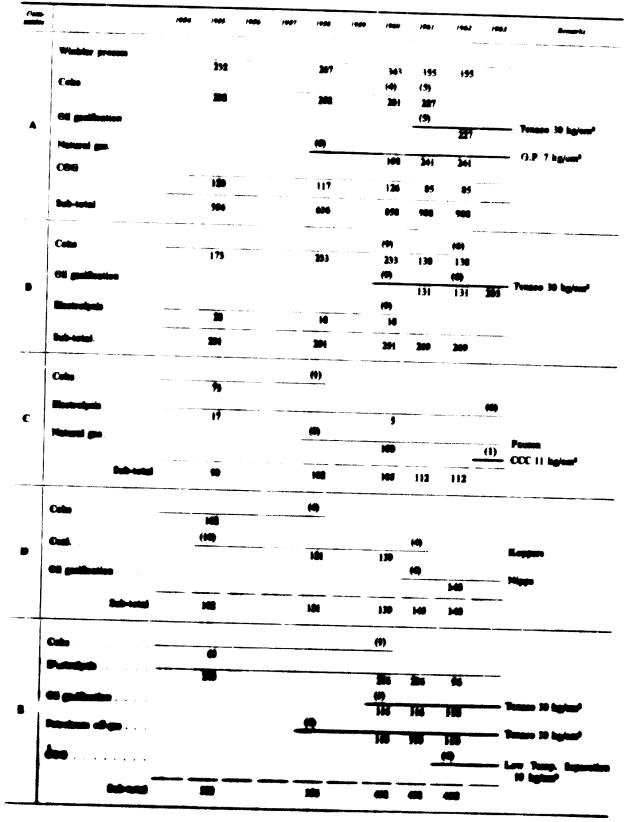
### D. Others

For nitrogen industry an advanced technical environment is quite essential. It requires chemists and engineers who have received a high level of training and workers who are well advanted. The construction and maintenance of the plant necessariate the co-operation of a highly developed mechanical and electrical industry. This point should also be hopt in mand.

At the beginning of the development of the ammonse industry in Japan, or in the period of its reliabilitation after the end of the Second World War, the Japanese povernment entended financial as well as publiced anontimor to the Japanese intragen industry Sirader assistance from povernment sources might be called for in set the development of introgen industry on the right track in developing countries.



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# TABLE 4. CRAMER OF STREEMEN SEARCE IN NHL PLANT (5/MP matrix ten per day)

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			/954	1935	1984	1937	1958	1939	1968	1961	1962	1963	Romarka
	Natural gas.								(12)				- COC 7 kg/em <sup>a</sup>
r		Sub-total	<b></b>	and the second second second second second second second second second second second second second second second					100	100	113		-
G	Natural gas.					(4)							- COC 7 kg/em²
<u> </u>		Sub-total					103		204	245	245		-
N	Natural gas.						(4)						- G.P. 7 kg/om²
		Sub-total							100	115	115		-
	Winkler proc						n						
	Kinstroly.is			87			75						
				95 (9)	(12)		106		106	196	196		
1	Oll garáfisatio		997 (MAR) 41			ar a ran gin hainan	50		130 (12)	149	149	999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 -	Ferner
	Notural gas.	· · • •								110	110		Power 15 kg/our <sup>a</sup>
		Sub-total		182			231		244	365	365		-
	Electrolysis.			37			42		42	42	37		
_	Oil gasifastia				(1 <b>2</b> )					(6)			<b>B</b>
1							62		42	(6)			
										64	107		Shell 30 kg/om*
		Sub-total		37			104		184	106	144		
	Cohe								(10)				
	Winkler proce Masterbais	<b>16.</b> – – – – – – – – – – – – – – – – – – –					*		*				
				45			34		34	34	34		
K	Oil gasifastio								(10)	165	105		Sumitone O.G.
ļ	Other gas						13		13	11			
		Sub-total		<b>%</b>			145		145		150		
	<b>Cebe</b>	· · · · -		100			123		123	(*) 120			
							(10)						Tonaso 30 kg/um*
L									105	M	114		
	<b>COQ</b>	• • • •									126		Low Temp. Reports
		- Tub-tutui		300			139	<del></del> -	*	207	296		
	Cit guilenties	)	<u></u>								(1)		Tangan 20 kaluar
	-	-											

TABLE 4. (Continued)

Com-1954 1955 1996 1957 1958 /959 1960 1961 1962 1963 Remarks (12) Oil meification N - Texaco 30 kg/cm<sup>a</sup> Sub-total 100 (2) **Oil multation** Ο Fauser Sub-total 121 136 140 140 (4) Coel. . . 232 310 199 166 152 P (3) Oil at - Texaco 30 kg/cm<sup>4</sup> 150 174 1.88 232 -tetal 310 300 340 340 (9) Cete . . . . 257 340 40 40 (4) . . . . . 23 (12) Q 01 - Sumitome O.G. 272 272 272 (4) (9) **G.₽**. 90 118 118 158 SBA Sub-total 200 430 430 430 430 (4) Winkler process. 121 30 50 (1) R COG + Ceal mine me 292 293 346 346 Sub-total 121 342 343 348 346  $(\mathcal{T})$ 84 71 71 71 (4) 8 56 \* 60 . 84 127 127 131 131 (7) COG . . . . . . ew Tem T 13 halant Bub-total 100 **ets.** . . . 41 45 7 12 12 U Oil gailte - Tennes 30 hajam<sup>4</sup> ð Ä 41 45 37 61 61 Total 2,498 3,547 4,304 4,698 4,894

TABLE 4. (Continued)

Plates : The figure in parantheses is the month of start-up or rist-down of the plant.

Protein under province.

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# 8. REALIZATION OF FERTILIZER PRODUCTION IN A DEVELOPING COUNTRY

Ing. Juan Ayllon V. and Ing. Jorge Otero R., Yacimiéntos Petroliferos Fiscales Bolivianos (YPFB), La Pas Co., Bolivia, and L. C. Axelrod, E. E. Bostwick and B. G. Mandelik, M. W. Kellogg Company, United States of America

### I. INTRODUCTION

In a country undergoing industrial development, there is a necessity to evaluate the ways in which the value of the gross national product of the country can be increased. Several schemes are usually considered to allow the optimum use of the available resources and achieve the greatest economic improvement within the resources available in this country.

The importance of developing food production in any given country is growing at the present time because of the steady increase in population in all countries and in particular in developing countries where there are special circumstances that favour population increase.

Therefore, there is a great need in most developing countries to provide fertilizers so that yields of crops in the available area can be improved. The Yacimiéntos Petroliferos Fiscales Bolivianos (YPFB) Company together with the M. W. Kellogg Company have made a study of these conditions for Bolivia. The study was guided by the fact that YPFB has four oil refineries in production and, therefore, the company's first interest was naturally to use the hydrocarbons available in Bolivia to improve the economic position of the country and enlarge its scope of production. A study was made to determine the production that could be based on the available hydrocarbons and a decision was made to investigate production of fertilizers. At this stage, the M. W. Kellogg Company joined forces with YPFB and a study was made of all the pertinent factors that could influence the decision of starting the production of fertilizers and decide on the size of the units most suitable for installation.

Details of this investigation are described in a paper by the same authors, propared for presentation at the ECLA Carness unseting 1-12 December 1964. In the present circumstances it is convenient to refer to that paper in order to describe briefly the factors that have to be examined before a comparative study is made between various approaches of the realization of fertilizer production.

The countries of South America contain 6 per cent of the world population and 5 per cent of the cultivated land of the world, but use only 2 per cent of the total fortilizers concurred. At the same time, the increase in the production of food is slower that the increase in population and in the period 1951-61 there was a decrease in *per capita* food production in this area. It seems, therefore, that there is a great necessity to establish production of fertilizers in this part of the world. In spite of this, only limited amounts of the resources available to the individual countries are being used for this purpose.

Although we naturally paid special attention to Bolivia, the way in which we approach the solution of the problem would apply to any country that is being developed industrially, wherever it is located, although there will be a great variation in climate and the influence of the geographical location in each country. For example, if it is necessary to import any raw materials, and if it is not possible to locate the production near the point where the imported raw materials are available at the seaport, then the cost of fertilizers based on such raw materials will be increased, and it may not be as economical to use such fertilizer components in preference to native raw materials.

The importation of raw materials has to be weighed against the over-all trade balance of the country. Study has to be is made to see how the production of fertilizers, once it has been attained, would change the economic picture. In our case, we realized that the advantages of decreasing the importation of food-stuffs into Bolivia would far outweigh the necessity to pay for the importation of phosphate rock. The possibilities of exporting some of the ammonium nitrate produced and some of the agricultural products that would be obtained with the use of fertilizers would easily pay for the cost of the imported rock. A study of the most important agricultural crops was made and the fertilizers most suitable for application to the soils in Bolivia were determined.

We were able to see that the products that require fertilizers most urgently are corn, wheat, sugar cane, and pastures which would need nitrogen, and potatoes, cotton, and rice which would need nitrogen and phosphorus.

The results available from the Bolivian agricultural experimental studies confirmed that there will be no necessity to import potassium, at least for a considerable number of years. We have thus been able to establish that the required fertilizer product will be NP fertilizers. Because of the fact that the phosphate rock has to be shipped from the seaports over the mountains, it is desirable that the content of  $P_2O_5$  in the finished product should be limited while high consumption of nitrogen nbould be stressed. The raw materials available in Bolivia are natural gas, oil, and sulfur. Economic analysis indicated that natural gas should be considered for nitrogen production, rather than oil.

### II. SUMMARY

This paper deals with the problem of establishing fertilizer production in a country where there is a necessity to improve production and at the same time conserve as much foreign exchange as is possible.

The case that has been studied thoroughly is the case of Bolivia and special attention has been paid to other countries of South America. The basic principles however should apply to any developing country regardless of geographic location.

Analyses of the economy of the country is made and the importance of agricultural production is evaluated. The over-all balance of trade is analysed. The climate and the soil in the principal agricultural areas are studied and experience with cultivation of the main crops is evaluated. Available experimental results are analysed and the probable need for fertilizers is established.

The most suitable types of fertilizers for the given area are determined. The possibility of exporting fertilizers or some intermediate products that can be produced in the fertilizer plant is evaluated.

A study is made of suitable locations of the fertilizer plants in the country taking into account the available means of transportation, the most economical delivery of raw materials to the proposed plant and the convenience of supplying with fertilizers the markets that will be established for them.

An analysis is made of the capacity of individual production units and several combinations of these units are considered so that economic analyses of the individual cases could be made. Several levels of production, several final products and several locations are compared and the economics connected with the realization of the several alternates is evaluated. The necessary investment, operating costs, and operating capital are discussed and an evaluation is made of the economy of the establishment of the fertilizer plant under consideration.

The investment costs for the various complexes is established and the costs of intermediate products and complex fertilizers under the individual circumstances is calculated. The cost of products delivered to the market is compared to prices established at the factory. The changes in the price structure of finished products due to the changing costs of raw materials are evaluated. Influence of the developing market upon the production economy is discussed.

### III. CONCLUSION

When an analysis is made of the available resources of a developing country, it is always important to pay full attention to all the individual factors in the particular country. Although the principles of the approach to the problem do not change, the circumstances under which the new plant will operate are always unique in a developing country.

The utmost effort should be made to utilize domestic resources. Attention must be paid to the price structure, that may differ from one country to another. The produced fertilizer must be suitable for the conditions of the agriculture in the area that will be serviced by the new plant. It must be distributed in such a manner that it will give maximum help to the farmer, and allow the manner of application which he is likely to prefer. The plant should be so designed that it would be the easiest to operate under the circumstances current in the selected area; it should be so located that the necessary services can be established economically, that the movements of products and raw materials will be convenient, and that the amount of product will truly correspond to the needs of the country, after proper allowance is made for the probable increase in the consumption.

### IV. DISCUSSION

Before making a more thorough review of the principles of designing a grass-root fertilizer plant in a developing country, it will be an advantage to quickly review some factors that apply to Bolivia, but may not be applicable to other countries, with regard to the building of fertilizer complexes.

Bolivia is a land-locked country, situated at a high elevation, and accessible only by crossing steep and high mountain chains. The connections to sea ports are by railroads, built half a century ago to serve the Bolivian mining industry. The original development was geared to mineral riches, and the national income depended on it. Since, at present, the main metal produced by Bolivia, tin, is enjoying a reasonably good market, the time seems to be opportune to develop other mineral resources.

Bolivia has some good agricultural soil located in the parts that are sparsely inhabited, and has a substantial concentration of inhabitants in areas where the soil is severely depleted and the climate rather unsuitable for agriculture.

It has, however, large resources of hydrocarbons, sufficient to maintain any industrial development that can be foreseen in a country with such limited and difficult access to the sea. There are possibilities of exporting certain products to the mountainous parts of the neighbouring countries. The soil is rich in potassium, and only NP-fertilizers need be considered.

Although it is possible that phosphorus deposits will be found in the country, this paper assumes that, during the first marketing period covered by this paper, domestic rock will not be available. Once we established the limits within which we should consider producing, we proceeded to determine what products would be most suitable for the conditions under which the plant in Bolivia will operate.

It seemed obvious that the final products should be available in bags so that the demand by small consumers could be satisfied. It does not appear probable that a market for bulk fertilizers will exist. The distribution of the products will no doubt be guided by the YPFB Company, at least in the original stages, before an independent network of distribution will be established. We have therefore decided to market bagged granulated products, for best warehousing and handling in smallvolume sales, and also for best distribution on fields by any type of distribution machine, or by hand.

The second consideration, that is specific for Bolivian conditions and cannot be generalized, was to minimize the consumption of  $P_2O_5$ . As it is desirable to limit imports into the country and, as at present there are no known sources of phosphate rock in the country, it seems desirable to be rather wasteful with nitrogen, while making sure that all the  $P_2O_5$  will be used. There is another reason for this approach: because of the great distance from the sea ports, the mountainous country, and the limited activity of the railways, a ton of  $P_2O_5$  in the product will cost, according to calculations that will be discussed later, around \$175, while a ton of N will cost only about \$110, reversing the usual price structure.

It is, then, obvious that a maximum of the  $P_2O_5$ in the rock that will be treated must be made available to plant life, and that only the absolute minimum of phosphorus can remain insoluble once the fertilizer has been applied. We have, therefore, rejected the possibility of decomposing rock with nitric acid: the pH in many Bolivian soils is quite high, and the danger of reversion to an unavailable form of calcium phosphate is quite substantial.

The thinking along the lines described led us to the decision that our product should contain P<sub>2</sub>O<sub>5</sub> either as superphosphate or as ammonium phosphate. As far as the nitrogen is concerned, we have examined both urea and ammonium nitrate. We assume, of course, that there will be a limited market for liquid ammonia application directly to the soil, and that the bulk will be consumed in solid form as a combined fertilizer. In our case, there is a strong inducement to produce ammonium nitrate, because in Bolivia there is a ready market for ammonium nitrate explosives. This market will be of great assistance in the initial operational stages, and will allow an easier period of initial ferulizer marketing. There is, however, a technical reason for our decision which is quite as important. In the manufacture of our granular fertilizers, 95 per cent ammonium nitrate solution can be used easily in granulation with superphosphate, or it can be made directly from nitric acid in the preneutralizer at the same time that ammonium phosphate is formed. It will not be necessary to prill the nitrate, and its use will simplify the granulation process. At the same time, the cost of the initial plant will be lower; this again in our case is important, as we are trying to minimize the initial capital investment.

As the transportation costs are quite high in Bolivia, it is necessary to consider as concentrated a fertilizer as possible, so that the cost of the product delivered to the farmer will not be unreasonably high when compared to the cost at the plant.

We have, therefore, studied two granulated products as basic fertilizer materials: a 30-15-0 and a 19-9-0 product. The first one would be produced by granulating the product of the reaction of nitric and phosphoric acids and ammonia, reacting with ammonia to completion in the granulator and recirculating part of the reaction product. This product can be produced in quite a few relative proportions between the N and  $P_2O_5$  by changing the recirculation and fresh feed proportions. A product with 42 per cent  $P_2O_5$  and only 21 per cent of N can be produced. This product would of course be used there, where there is a need for a predominantly phosphate fertilizer.

To manufacture 19-9-0, highly-acid superphosphate will be produced. The superphosphate is introduced into the granulator directly from the superphosphate den, without any intermediate storage for curing. In the granulator, the excess acid in the superphosphate is neutralized with ammonia and this reaction product is simultaneously granulated with a hot, concentrated solution of ammonium nitrate. This scheme, although producing a less concentrated final product, has the advantage of a cheaper P<sub>2</sub>O<sub>5</sub> source plant, and of easier operation, eliminating the problem of disposing of the calcium sulfate filter cake from phosphoric acid manufacture. When the production cost of ammonium nitrate is determined, it is also seen that in this case it is possible to produce it more cheaply. Should the demand for the ammonium nitrate for explosives increase more quickly than for fertilizers, it would be very easy to produce it rather than a fertilizer, as the concentrating equipment will be available. A thorough examination of all the aspects of the problem has to be made, as the advantages of one system are in close balance with the advantages of the other one.

Next step in the study was to determine the sizes of the individual plants forming the whole fertilizer complex. The basic unit, and of course the most expensive one is the ammonia plant. For 20,000 TPY of N the plant would produce 77 TPD of ammonia, for 30,000 TPY it would produce 114 TPD. At the minimum expected consumption of 15,000 TPY, the daily requirements of ammonia would be 57 TPD. We have therefore considered the possibility of suggesting an ammonia plant of 57 TPD that could be duplicated at a later date, a 75-ton plant and a 100-ton plant, the last two "pushed" to the required capacities by making the necessary compressor and heat exchanger adjustments. A thorough examination of the cost of the respective plants led us to believe that in our case it will be the most economical solution to design a plant specifically for the given task, so that we will have a unit that can be easily operated by personnel who by necessity will have only a limited training background. We have therefore made preliminary designs for the 77 and the 114-TPD plant, and included the prices for these units in our study. Ultimate decision will be made by the management of YPFB, when they will weigh the capital cost against the returned profits, and decide whether to build the smaller or the larger complex.

The size of the nitric acid unit will vary according to the final product selected. In the more concentrated final product, some of the ammonia is fixed as ammonium phosphate, and thus the need of nitric acid is lower than for the 19-9 product, where all of it is in the form of ammonium nitrate with the exception of the small amount of ammonium sulfate produced by neutralizing the excess sulfuric acid in the superphosphate. Thus the sizes of the nitric acid plants proposed are 117 and 167 TPD for the first fertilizer, and 132 and 200 TPD for the second fertilizer scheme.

The same reasoning applies to the sizes of the sulfuric acid plant. The respective sizes would be 70 and 117 TPD of sulfuric acid, and 52 and 82 TPD. The plant would, of course, use the domestic sulfur, which is abundant and of excellent quality. The cost of the sulfuric acid plant will thus be rather low. Here, again, we are faced with a special Bolivian aspect. There may be countries where sulfur will be available as pyrites, thereby making the plant substantially more expensive, or the sulfur will have to be imported, and some restrictions may be desired in producing sulfuric acid. However, in the case of Bolivia, the acid can be produced at a cost of about \$18 per ton of H<sub>2</sub>SO<sub>4</sub> and therefore there is an inducement to make it.

The phosphoric acid plant, which would be part of the complex of the more concentrated fertilizer production, would have a capacity of 26 or 44 TPD of  $P_sO_s$ . The highest quality rock should be used, as the premium for high quality is much less than the cost of shipping the rock to Bolivia. The acid would be produced as 31 per cent  $P_sO_s$  acid, and used directly in the granulator after being neutralized by ammonia in the premix tank. This is the cheapest method of operation in a small plant, and a quite easily controlled one. The granulation section will, of course, operate with a substantial recirculating ratio.

The use of phosphoric acid and ammonium nitrate in the granulator has the outstanding advantage that a great number of fertilizers whose analyses vary widely can be produced. The main disadvantages of this approach are that it is more expensive, and that it is necessary to use certain corrosion-resisting materials that are easily damaged.

The superphosphate plant which is used for the production of the 19-9 fertilizer is very rugged and very easy to operate. The daily capacities for this plant will be 130 and 220 TPD. The superphosphate will be produced in granulated form. Some of it will be sold directly, and the rest will be used directly from the den in the granulator to obtain a granulated complete fertilizer product by adding ammonium nitrate and neutralizing with ammonia. It is, of course, possible to use prilled ammonium nitrate, rather than a solution, but over-all production economy favours providing the nitrate as a concentrated solution.

The ammonium nitrate plant would consist of a largesize solution unit, producing the solution suitable for introduction into the granulator, and into a small prilling tower for the production of prilled fertilizer and explosive grade ammonium nitrate. This feature again is specific for Bolivia and countries with developed mining industries. The over-all picture has to be fully evaluated in the case of every possible location of a fertilizer complex. We shall, of course, produce the explosive grade ammonium nitrate as we would have substantial inducement in marketing it.

The granulation plant size will be a function of the amount of the planned product and its concentration. In our case, the capacities will be 160 and 240 TPD and 260 and 390 TPD. The plant will granulate the desired product, maintaining a required ratio of resirculation. and producing a fertilizer ready for bagging. In all cases the heat of neutralization will be used to evaporate the excess water introduced with the feed materials. As a granulation plant is rather inexpensive, the size of this unit is not of major importance.

Since we have to consider building the plant in locations where only limited facilities are available for any industrial production, the cost of the off-sites will be of major importance in all the cases. The location of the plant is important not only from the point of view of the supply of the raw materials to the plant, and the case and cost of marketing the finished product, but also from the point of view of the initial cost of the auxiliary production facilities, that is, storage, steam, power, and cooling water supply. In the case of our project, with the over-all price somewhere between 10 and 15 million dollars, the location of the plant may change the price of the erected facilities by as much as \$1,000,000. Great care must be given to the evaluation of all the important factors such as accessibility of the plant site, soil bearing, water availability, etc. In our case we have selected four sites for final evaluation. Two of them are adjacent to two of the refineries at Santa Cruz and Cochabamba. The other two sites, at Pojo and Camarapa, where at present there is no industry, but where natural gas will be available at a low cost through a pipe line, are near the main road from Cochabamba to Santa Cruz, and therefore would be accessible by means of trucking.

The great advantage of the Cochabamba site is that phosphate rock could be shipped there directly by rail, without transferring it to trucks. It is also situated in the centre of the country, at the hub of all the communications, and all the ultimate markets could be served from there without transshipping the products from rail to road, or vice versa. It is situated conveniently to the Altiplano region, which must be sooner or later supplied by fertilizers to improve the very poor crop yields in that section of the country. There is, however, no natural gas available there, and the crude oil cost is substantially higher in Bolivia than the cost of natural gas. It would, therefore, be best to produce ammonia at Santa Cruz, Pojo, or Camarapa. and ship it to Cochabamba for the production of nitrate and finished fertilizers. Phosphate rock and sulfur can be easily delivered to the Cochabamba site. Shipping of ammonia is the cheapest way of moving the nitrogen, as the N content in ammonia is by far the highest of all nitrogen-bearing fertilizer materials. A suitable number of tank trucks can be easily purchased, and the shipping of one ton of ammonia from Santa Cruz to Cochabamba will cost about \$10, including maintenance and amortization of the trailers. For the total fertilizer production that is considered, the amount of phosphate rock requiring shipping is somewhat higher than the amount of ammonia that would be shipped, and there is thus a great inducement to ship ammonia rather than the heavier rock. Here, again, full attention has been given to the local conditions.

We believe that every project in a developing country should be studied thoroughly by an engineering contrator, and a plant that fitts best into the local picture should be supplied. The conditions in such a country are always quite specific, and no attempt should be made to introduce standardization there, where only one plant is being built. In a developed country it may pay to build a plant best suited for a production of a round number of tons, say 50 or 100 tons per day. This should be avoided in the case of a developing country, as it may not be possible, for many years to come, to sell excess capacity of a given chemical, even at a lower price, than the one considered for the chemical where it is treated as a fertilizer intermediate. The wasted utilities, or the extra effort required to run at an unwanted capacity, will in the end outweigh the advantages gained by engineering standurdization.

When deciding the type of drives for the ammonia plant compressors, we evaluated steam, gas engine, and electric motor drives. We found that the most economical drive is the gas engine. Here, again, the cost of fiel, cooling water, and the original cost of the installation must be considered. Some steam will, of course, be produced in the ammonia plant, and some small drivers will be electric motor driven, but the large drivers will be gas engines. In the nitric acid and sulfuric acid plants, the main compressor will be driven by waste heat boiler steam and small drivers will be electric. Excess steam from the acid plants should provide the necessary small amounts of steam for the nitrate and phosphoric acid plants. It will, however, be necessary to have a stand-by package boiler should the acid plants be at a different location than the ammonia plant. Steam production in the acid plants is regulated entirely by the rate of production, and adjustments possible in an ammonia plant steam production in the primary reformer cannot be made.

The finished product storage facilities have to be located at various points throughout the country. Decause of the limited facilities for transportation it will not be advisable to store great quantities of the fertilizers at the plant, and iry to ship them all out during the fall and spring fertiliz-storage buildings, in addition to the one located at the producing plant, in the regional centres of the country, from which the farmers could be easily supplied at short distances. In our case we selected La Paz, Oruro, Sucre, Cochabamba, Tarija, and Santa Cruz. Should the entire production be located at Pojo or Camarapa, an additional storage facility would be needed at these locations. Here, again, we are guided by the present-day availability of trucks and road facilities, and this situation many be different in another developing country.

Particular attention must be paid to the water that is available. For an ammonia plant the process water is actually the boiler food water, and this must be sustable for boilers of at least 450 psig operating pressure, and preferably 550 peig, so that the optimum reforming pressure in the ammonia plant can be reached. In the mitric acid plant, the boiler can operate at 250 psig, and the process water should just be as free of chlorides as possible. The water must be of such quality that no deposits would form in the coils of the absorption tower. For the sulfuric acid plant, water suitable for a 230 paig boiler will be sufficient. The process water should be free of Ca and Ba to avoid precipitation of sulfates in the process lines. In some of our losstions, there will be a noce to use quite an elaborate water treating sch ome which ans that when the total cost of an installation at one

location is compared to that at another location it is important to include the water-cost evaluation.

When we were establishing the cost of individual intermediate products of the fertilizer plant, we tried to obtain the cost of the product as close to reality as possible so that we could obtain a guide for the evaluation of the final scheme. At the same time, this guide aided in determining what other industrial production might be attractive in Bolivia that could use the chemical intermediate compounds, produced at an attractive price, in the fertilizer complex. It will always be an interesting approach to explore all the possible uses of new intermediate products that will be available in a country for the first time, to see if attractive schemes of use for them may be found. In this way, the original investment for fertilizer products can be reduced.

In our case, we have examined the cost of the product as a function of changing price of the natural gas. We selected limits of 12¢ and 30¢ per 1,000 standard cubic feet for our investigation, and plotted the prices of the intermediate products as functions of the changing price of the natural gas. In all cases this relationship is linear. The effect of a rising price of the gas is cumulative, however. For example, the price of ammonia varies from \$44 to \$62 per ton, while for ammonium nitrate the variations are from \$39 to \$73. That is, a ratio of 1.4 grows to 1.9. The more steps that are involved in the preparation of the final product, the greater will be the ratio increase. This approach is very important, as in Bolivia at present there is no consumption of natural gas, and it is necessary to create a suitable price structure for this raw material.

The prices are established for the other raw materials, phosphate rock and sulfur. While it may be possible to obtain the rock at around \$8 per ton at the sea port. the cost of shipping it by rail to the centre of Bolivia will amount to about \$28 per ton. It is obvious that the only important fluctuations of price will be those caused by possible changes in the shipping rates from the sea port to the point of use in Bolivia. No other changes could be really significant. As far as sulfur is concerned, its price depends on the export price that can be charged in Chile, since small amounts are actually exported at present. Here, again, the limiting factor will be the high cost of shipping, and the price will be quite close to the world price, since the market in the mountains of Chile and of the Argentine can consume some of the available sulfur. It seems probable that the present-day price of around \$28 per ton will not change to any considerable extent.

Small changes in the price of the finished products due to the changes in the prices of the two raw materials were studied, but no final conclusion is available. It seems certain that the expected changes in the price structure will be of very secondary importance.

The cost of various kinds of bags was investigated, and their value in the used bag market in Bolivia was evaluated, so that we could affer the product to the farmers in an attractive and economical package. The bag closing and handling methods were evaluated with the particular local needs in mind. Shipping costs within the country were investigated. It is not always easy to find a reliable source of such data, as up to the present, no doubt, shipments of goods from one place to another were influenced by factors that are not similar to our needs. In many cases, it will be necessary for the producer to ship materials by his own trucks to avoid delays and obtain a reliable economical basis for a future development of the commercial shipping of fertilizers.

The prices for the products at the factory give us only a partial picture of the whole problem. We must also know the prices of the product at the place where it reaches the farmer. A picture of such prices for various locations in Bolivia was established. As a basis for locations, the five localities mentioned previously were selected. It can be assumed that the farmers would be able to purchase at such a location, or that the services of distri-buting the products bought at such a centre would be provided by some local authority in the original stages, to facilitate market penetration by the final produ It is quite difficult to approximate the cost of the faal stop of distribution, as it will be influenced by many qu ective aspects. From the data that we obtained by our calculations, we hope to be able to provide enough information so that the management of the YPFB Company can decide whether it will want to start a it equalization scheme, or sell at prices that include the actual shipping costs as these vary from one locality to another. It may very well be an advantage to sell at the same price in all of the six warehouses of the company, and take care of the varying costs by a compensation schome.

A comparative analysis was made for the cost of shipping raw materials and the intermediate and finished products to a given location. The necessary facilities at such a location were included in the established cost. This analysis will facilitate the final decision of the YPFB management to decide upon the manner in which the product transportation should be handled.

It must be expected that once the production of the fertilizers is established, it will not start at too high a level, but must follow the demand and the customs of the local farmers. Although the need for fertilizer consumption is very great, it will be necessary to overcome the initial obstacles in the marketing of the products. How the farmers will be educated is a problem that is at prevent being investigated by the Bolivian Government and by the YPFB Company. Suitable inducements are being analyzed at present, and the final decision will no doubt be a result of the co-operation of the YPFB management and the local pertinent authorities.

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# 9. NATURAL GAS RESERVES IN MEXICO AS A FACTOR OF THE SOCIAL AND ECONOMIC DEVELOPMENT OF THE COUNTRY BY MEANS OF NITROGENOUS COMPOUNDS

### Petróleos Mexicanes, Mexico

### I. INTRODUCTION

Petróleos Mexicanos (Pemex), by being an integrated petroleum institution, and now also a petrochemical institution, plays a very important part in the economic development of Mexico. The development activities of Petróleos Mexicanos have been oriented to benefit all the evels and sectors of the population. The great achievements in industrial development in Mexico have caused an unbalanced situation between the two most important sectors of the country, the industrial one in full prosperity, and the largest sector, which is the agricultural population, in a depressed situation. In order to correct this imbalance, Petróleos Mexicanos has developed this programme, by means of which it is expected that the agricultural and rural sectors will receive the benefits of integrated development.

With regard to the real and current situation of the agricultural and rural sector, the outstanding problems are the following:

(a) Low agricultural productivity;

(b) Low income;

(c) Low purchasing power;

(d) A large proportion of the population is in this sector, approximately 61.5 per cont.

These problems have resulted in a depressed situation and can be summarized as follows:

(a) The agricultural sector has a very low income and very limited funds at its disposal;

(b) The lack of income and funds results in a lack of technology, furtilizers and irrigation;

(c) Thus the agricultural sector cannot increase its productivity, on the contrary, its average yields are decreasing since the food elements of the sell in Mexico are being exhausted;

(d) As a result of this decreasing productivity, the agricultural sector cannot increase its sales and consequently its income.

A great deal is being done by the Mexican Government to correct the situation; however, its efforts consist entirely of long-congo programmes which estail big investments and, as a consequence, great risks.

Petroleces Mentionees is proposing to contribute to the correction of this situation by applying a more intensive technology and promoting a wider use of fertilizers. These proposals can be implemented in a short period of time and, in consideration of the low income of the agricultural actor Petróleos Mexicanos proposes to make ammonia and nitrogenous fertilizers accessible to the agricultural and rural sector, at prices considerably lower than at present. Reduction in the price of ammonia by 30 per cent is being suggested. It is obvious that the combination of several factors results in increased agricultural productivity (seeds, soils, rain, fertilizers, insecticides, etc.); however, it can be stated in general terms that the factor susceptible to more rapid control is fertilizers. By using a greater amount of fertilizers, farming productivity will increase in a short time.

Several means are being proposed by which Petróleos Mexicanos could reduce the price of ammonia and nitrogenous compounds. However, the one which is bound to produce the greater impact is the construction by Pemex of ammonia and urea plants with the greatest capacity that can be built at the present and by the utilization of the most advanced technology in the manufacture of fertilizers. This proposal calls for the construction of several large tonnage ammonia and urea plants, the capacities suggested being 1,000 tons per day of ammonia and 500 tons per day of urea. Large plant capacity will result in lower operating costs and lower sales price of fertilizers to the farmers in Mexico.

Of all the food elements in the soil of Mexico, the most important is nitrogen since it is being exhausted from the soil and also because of the lack of organic matter to replace nitrogen. Therefore, the main part of the petrochemical development is to construct plasts that produce anhydrous ammonia as the most insupensive and simplest of all nitrogeneous compounds, and the one with the highest nitrogen context.

Ammonia is made from nitrogen and hydrogen. Nitrogen is available as a constituent of air and hydrogen is obtained from hydrocerbons. Matural gas is the hydrocerbon to be used in the large production of ammonia. Therefore, natural gas is a basic row material in the production of ammonia and thus has a fundamental part in industrial and agricultural development, since by the wider use of natural gas for the manufactures of ammonia a great contribution is made towards inscending farming productivity.

### II ORMERAL INFORMATION

For the development of this survey, the following criteria were used

(a) Situation of the agricultural sector (1998-1988) and its forecast without the implementation of these proposals.

(b) Situation of the agricultural sector and forecast with the implementation of these proposals

(c) The bonefits to the country

As distated by the Messean Constitution, in the Petrochemical Law Article 27 only Government enterprises can carry out the first transformation of petroleum products to petrochemical products.

Hydrous ammonia fails within this legal juriediction. For this reason, Pomon will construct and operate the ammonia plants proposed it is also considered that Pomon, by means of the implementation of these proposals, obtains for the country the following leading

(d) By measurporting in the agricultural sector a larger propertion of the economically active population, a wider market for fuels and lubricants will be created since this sector will domand an over increasing amount of capital and some-capital goods (trucks, cars, tractors, form machinery).

(b) Petróleos Mexicanes will make an effective contribution in reising the level of techniscal and administrative knowledge in the agricultural sector Such knowledge is indispensable for a wider use of modern agricultural equipment and methods.

(c) The wider use of modern agricultural methods will demand a large number of chemseal compounds (incerticides, horbitides, soil improvers, PH controllers, etc.). These chemical compounds ortid by produced within the sphere of the petrochemical industry, generating in this way an increasing domand for products from this industry.

(d) A higher income in the agricultural sector and a greater domand in this sector for all binds of goods and services will provide a wider and more secure market for industry in general.

III. Analysis of the specificate attraction of the addition trade sector in Manco these 1960-1960 and persecutive to the year 1970 wellow the adjustmentation of the proposal to medical addition type.

In this castion are presented the statistical data on the optimizational castor for the period 1988-1988 and with this data forecasts ware made up to the year 1978 without considering any operation for the improvement of the eccentricity fortune of the periodical party.

### A. Rural and furning psychotom

These data were divided into four brand entrypoles:

### 1 Statistical data in population

1 - 1 <b>9</b> 4	Protest engestantion	Papalistan di antika di 1993, Silit da antika antikakto ganta	Population constituent as raeat and capticultural
1940	19,653,352	4, 105,690	15.346,868
1950	25, 791,017	7.453,001	+8,337 986
1969	<b>34,98</b> 5,120	12,379,201	20, 545, 888
1985 4	19,3 <b>95,88</b> 0	15,300,235	23,832,765
1970 -	45,468,680	19,637,300	36,090,700

1965 and 1970 are command from the forecasts of and registros

As can be observed, the rural and farming population for 1970 will form 61 per cont of the total population. thus it is obvious that this sector will have a great influence on the connon y of the country. It can be expected, also, that Monsoo will not be able to reach a high degree of industrial development if the internal market is not first developed by increasing the purchasing power of the large rural and agricultural sector. If this situation is not improved, the agricultural sector will not be a wide enough market and as a consequence there will not be enough reductrial domand, there will also be a large unbalance between the contribution of the agricultural and industrial sector to the gross antional product. This situation will erents great economic problems since the low productsvity of the agricultural sector will be an additional load on the productive sector. The above-mentioned situation will create also political and governmental problems because the burden of the agricultural sector will be a load to the National Treasury and to the Federal Government. The low measure of the agricultural sector will also create sectal problems by being compared to the properous and highly salaried industrial sector.

These conditions will be observed in grutter detail in the following sections.

2. Income and productivity of the agricultural sector in the seried 1950-1960 and its projection to 1965 and 1970

The following tables have be a prepared giving the statistical data on the group national product from the period 1958-1963, based on information provided by the Bank of Monico.

- 1 Grees antional product by sectors of autovity 1980-1963, in million passes of 1980;
- Indires of gross national product by assess of antivity 1980-1963 (1990 prime).
- Contribution in percentage of the different sectors of artivity in the gross antional product 1980-1968 (1990 prices);
- Gross antional product by sectors of activity 1988-1968 (in sufficen passes of 1988);
- 5. Indians of gross national product by sectors of antivity 1988-1963 (3988 primes);
- 6. Contribution in processings of the different maters of antivity to the group mathemal product from 1005-1000 (1000 prices);
- Arrange make of generatio of the genus canimal perdust by contrast of authoby 1000-2000 (1000 press);

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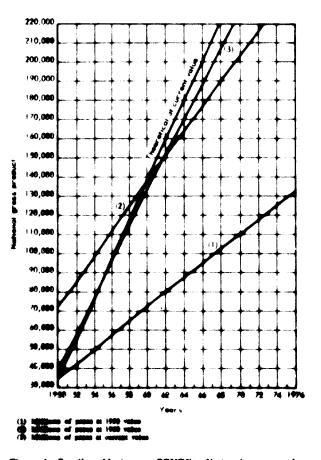
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### TABLE 10. PROJECTIONS OF THE TOTAL NATIONAL PRODUCT AND BY SECTORS OF ACTIVITY, FOR THE YEARS 1965 AND 1970, OF EACH ONE OF THE PREVIOUS TABLES

From the statistical data shown in each one of the previous tables of the gross national product and by sectors of activity, estimations were made of the projections of the trends for the years 1965 and 1970, with the following results

Table protocood	( <b>96</b> 3	/970
ł		
(a) Total antional gross product in		
million peece of 1950 (\$) Grees national product for the	92,000	110,300
agricultural asstor in million		
peece of 1990	10, <b>00</b> 0	1.2,160
2.		
(a) Indi. 5 of gross national product in 1930 prime	219.5	356.5
(b) indices of national product of		
the agricultural sector in 1950 entres	183	211
	14.3	
3 Contribution in personnage of the agricultural sector to the		
gross splicant product in 1990 prizes	11.7	10.5
4	,	PO. 3
(a) Total gross national product in		
million passe of 1980	171,000	200,500
(b) Gress national product of the agricultural sector in million		
passes of 1960	16,780	18,500
<b>\$</b> ,		
(a) Index of the total gross antional grodest in 1960 prices	129.2	
(b) index of the gross national pro-	144.4	14 <b>6</b> .0
dust of the agricultural spater in		
1960 prices 6. Contribution in percentage of	115.0	138.0
the agricultural sector in the		
iutal gross national product in 1980 prices	•.7	8.5
7	•. /	•.9
(s) Average growth rates of the		
gross national product in 1989		
prises (d) Average growth rates of the	4.4	4.9
gross autional product in the		
agricultural anotar in 1960 points	3.0	3.79
8. (a) Tatal man anti-mai an-dust in		
an in second management in the second management with the second se	178,689	<b>339,659</b>
(4) Grass assignat product in the		
agriculturaj easter in corrent saj- line pour	18.600	31,000
9. Contribution in personnego of		
the agricultural states to the		
talai geno addenad product at extent pipe	-	



Piguro 1 Pereduce Mentanne (PENEX) Mattemat gross product of Manton (million passe)

- Gross national product by sectors of activity 1950-1962 in million passes of 1963;
- Contribution in percentage of the different sectors of activity to the grees national product 1950-1962 at ourrent prices of 1963.
- Personal of tables 1, 2, 3, 4, 5, 6, 7, 8 and 9 for 1965 and 1970 for the total and for the agricultural center

All the statistical data and the projection trends are chosen in graphic form in the following figures 1, 21, 101, PV and V

3. Average perchasing power of the agricultural sector

In order to apply the overage perchasing percer of the applications matter through covered years, the statetion of the propagational product will be related to the rared and applications population

 Behavioralize and influences of the agricultural sector on the contemp

In order to present the stati allustics of the country and thus the minimizing of the agricultural easter on the

		1940	1965	1976
(a) Aveng	perstanting pe	wer in prices of 19	50	
ress national product of the agri- endiment sector in million pass of				
1980	5,999	9,178	10,000	12,100
ural and agricultural population in the unando of infinibilitants	16,330	22,544	23,893	26,031
watego purchasing power of the agricultural sector per capits and				
per year	397.1	407.1	453.1	464.8
(b) Average	purchasing per	er at prices of (	900	
ires national product of the agri- militaral sector is suithen pass of				
1960	9,477	14,496	16,700	18,500
werel and agricultural population in thousands of inhabituate	18,338	22,544	<b>23,8</b> 93	36.091
verige purchasing power of the agricultural series per agrics and				
per year	516.8	<b>645</b> i	700.7	710.7
(e) Ananaga	purchasing per		<b>100</b>	
ross autional product of the agri-				
panan.	1,999	14,488	16,000	31,000
well and applicational population in the use of industriants	16,388	38,544	25,805	36,091
anter provincing power of the approximation of the sector per capito and				
fit year	387.1	<b>648</b> . i	798.3	885.7

(a) Tuble /

CANES HARRING, FAILURY OF THE ADDITIONAL METHOD IN MEMARIN PURS IN \$100

A gritté contrast la obtervail in the following data giving the comparison between the purchasing grows of the agricultural arter and the object casters related to industry and containers.

	1000			
i) Tetal grap satisma product i) Grap satisma product of the	44,000	14,247	10,000	110,500
agelandburd antior 19 Group ageland product of up -	1,000	9,278	10,000	12,100
ters-eduted with expension and industry # Payndistan of the ageingingsi	36,000	<b>61,109</b>	01,300	10,400
nater is designs of is- lables. Papalates of the ether same	16,300		<b>30,000</b>	
b ihmanab of bilalitans. Antras patients pour of	1,484		16,00	19,000
Co-opticitant casto pr cysto est par pro Arrango particular prov d	<b>307</b> .8	<b>49</b> .8	48.1	-

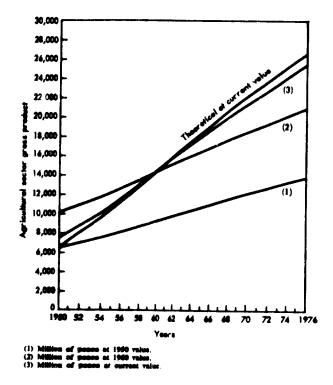


Figure II. Petróleos Mexicanos. Agricultural sector gross product (million pesos)

economy, the following comments are presented in relation with the forecast of the statistics given before.

### (b) Comments:

There exists a great difference between the purchasing power of the agricultural sector and the purchasing power of the other sectors, this difference being of the order of \$4,000.00 pesos per year and per inhabitant, in favour of the sectors related to industry and commerce. It is evident that this difference should be reduced considerably for the following reasons:

(i) To increase the purchasing power of the agricultural sector becomes imperative, otherwise a political problem may result, considering that the larger percentage of the population has this very low purchasing power.

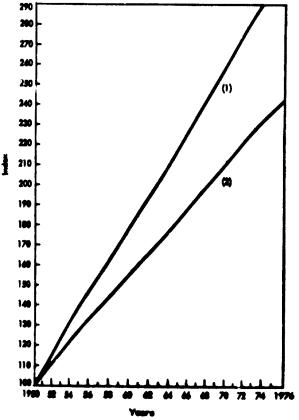
(ii) The daily average income of the agricultural sector is approximately 30.90 pesos per inhabitant in 1930, an amount which is not enough to meet their minimum and basic needs. The daily average income of the other sectors is around \$13.00 per capits in 1950, an amount which is at least sufficient to meet their most pressing needs.

(iii) The various programmes which are being implemented to increase agricultural productivity will not yield the desired results. It is estimated that by these programmes the daily average income per capite of the agricultural sector will increase from 30.90 passes per day in 1930 to \$1.27 passes in 1970.

(iv) It is pointed out also that the purchasing power of the other sectors is of the order of \$5,000.00 pesos per inhabitant per year, and that this amount has not increased noticeably in the past; on the contrary, one can observe a decrease in this purchasing power. This is explained by the fact that the sectors related to commerce and industry have lost their power of growth and are beginning to show a decline in their income. This is caused by the limited demand for all sorts of goods by the agricultural sector from those sectors connected with commerce and industry. Therefore Mexico faces a situation in which the depressed condition of its agricultural sector is beginning to exert a downward trend on the incomes of the sectors connected with industry and commerce. It is evident that in the over-all economic planning of Mexico further progress will become increasingly difficult if the problem of the low agricultural productivity is not resolved soon (see sections I (Introduction), and II (General information)).

### (c) Tables 2 and 5

In order to make comments on table 2, it is necessary to relate it to table 5, in which are shown the indices of



<sup>1)</sup> President States (States)

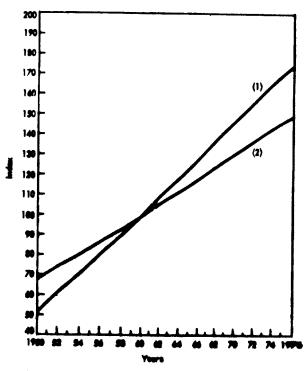
Ageno III. Petroleces Messicanes. Index of the national press produces and of the agricultural sector at 1950 prices (1950 = 180)

gross national products by sectors of activity with two different bases:

(i) 1950 = 100(ii) 1960 = 100

In order to make comments and comparisons of tables 2 and 5, we will have as a base the growth of population in Mexico, which is 3.2 per cent per year. Therefore, the minimum possible in order neither to lose nor to gain money (operate at the point of equilibrium), considering base 1950 = 100 and 1960 = 100, will be in 1951 and in 1961 of the order of 103.2 the index of each activity, indicating thus the (+) gain money, and the (-) lose money.

	ndi:	-								1951	1 <b>961</b>
Total gross nativ	on	<b>N</b>	p	ro	du	ict				107.7 (+)	103.5 (+)
Agriculture										105.0 (+)	102.6 ( )
Livestock breed	ine									107.1 (+)	103.9 (+)
Forest production	20									1G1.5 (-)	89.8 ()
<b>Fishing industry</b>	1	•								94.8 (-)	108.1 (+)
Mining		•		•						96.4 (-)	95.8 ()
Petroleum	•									110.0 (+)	111.4 (+)
Manufacturing										110.6 (+)	103.6 (+)
Construction .	•									109.5 (+)	101.0 (-)
Electricity	•									111.1 (+)	109.5 (+)
Transport			•							109.6 (+)	100.7 (-)
Commerce	•									109.7 (+)	103.2
Government .	•		•							106.5 (+)	107.3 (+)
Other activities.	•		•		•	•	•	•	•	103.9 (+)	104.7 (+)





Pipers IV. Petrollous Mantanas. Julius of its sational proce produce and of the agricultural scoter at 2000 prime (2005 - 200)

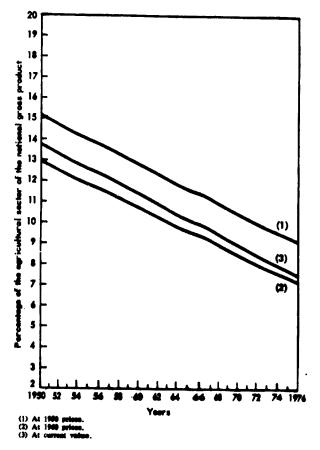


Figure V. Petróloos Mexicanos. Perosnage of the agricultural sector of the national gross product

This brings out the fact that in 1951 three sectors of activity lost money (forestry, fishing industry and mining) and in 1961 five sectors of activity lost money (agriculture, forestry, mining, construction and transport) and during 1961 commerce was just in equilibrium. We must consider also that the total gross national product in 1951 was 107.7 the total index, and in 1961 the total gross national product was 103.5, nearly at an oconomic equilibrium point in the country and in process of decline. That is why it is important to stress once more that it is fundamental, in order to recover the process of economic growth of the country, to incorporate the farming and rural sector of the country to the economically notive population, creating in this manmer internal markets and eliminating by means of increased agricultural pred tivity the great difference in purchasing power betw the agricultural sector and the other sectors of the e nomy and also decreasing the related social, p and economic problems.

### (d) Table 3

As can be observed, the contribution in percentage of the agriculturnal syster to the testal gross national predect of the country has the following statistical tradency.

	1 <b>930</b> *:	1955 V	1948 No	/965 "1	1970 **
Total gross national product	t <b>00</b>	100	100	100	160
Contribution of the agricultural sustor	14.6	15.2	12.3	117	10.0

This table brings out the fact that the contribution of the agricultural sector le the gross national product is decreasing. Considering also that the population of the agricultural sector is increasing considerably, it is evident that an economic crisis of major proportions is developing. This crisis, if it materializes, will depress the social, economic and political activities of the country, which has achieved a great stability through prolonged efforts of all the sectors of the sconomy. This expected crisis

could well be avoided if intensive and forceful efforts are carried out in order to increase agricultural productivity

### (c) Tables 4 and 6

From these tables we obtain the same conclusions as from tables 1 and 3, except that by being presented st prices of 1960 we find the same tendencies but with a slight overlap in all the data, as follows

	1950	1988	1965	1970
(i) Total grass national product un millions of pass	77, <b>01 5</b>	t <b>40, j 46</b>	171, <b>500</b>	<b>J0</b> 3, <b>580</b>
(ii) Gross national product, agricultural sector	9,477	14,498	i <b>6,780</b>	18,500
(ili) Ores national product, other sectors	67,538	125,679	154,888	185,000
(iv) Population, agricultural sector	18,337,926	22,548,888	23,832,765	26,838,768
(v) Population, other sectors	7,453,891	12,379,241	15,560,235	19,637,240
(vi) Purchasing power, agricultural sector pri replie per year	516.20	643 10	798-78	710.78
(vii) Purchasing power, other spotors per- applie, per year	9,061 . 80	10,153.40	9,955 <b>60</b>	9,430.98

However, in 1960 priors, which are the closest to the current ones, the problem is presented in a more acute manner since if we observe in comparative form the contents of tables I and 4, we will see the following

(iii) /960 prizes

Average purchasing power of the agricultural sector per- equility and per year in 1960 prices.	316.20
Average purchasing power of other sectors per capite and per year in 1960 prices.	9,061.00
Difference is purchasing power	1.544.00

Parahasing power of the spisultural sector in 1950 prices.	- 327 H
Purchasing power of the spiniture sector in 1988 primes.	<b>916.20</b>
Parahasing power other auton, in 1950 privas.	4,704.30
Parahasing power other exten, in 1989 pelace.	5,001.00

This brings out the fact that while the purchasing power of the agricultural source is 1960 prices incorrespond by an overage of \$100.10 press, is the source purchasing power per capita, yearly, the other sectors reserve an increase in 1960 prices in their source purchasing power per capita, per year, of the other of \$4,357.60 press. Thus the following differences is the purchasing power are observed.

### (i) 1950 prime

Average partilating power of its spin-strangt survey per aspits and per year at 100 pipe.	
Arrange purchasing power of other values per capitor and per year in 1980 polars	
Billionno in purhain prover	4.777.50

e we observe that tables 4 and 6 show the s ns of the agricultural sector as the case shows in ible 1, with the enception that this proj m is p In a much more souls monmor since tak ins 4 and 6 am in primes of 1960; also, it is instarent hg to poi nt ant that he duity everage means per capita of the s or in 1960 prices is of the order of \$1.41 ina far 1958, and in twenty years (1978) will reach \$1.95 p ---day. As a point of reli rease and to show shorty th in ai non of the motor, the price of a litre of mult in \$2.20 m love the incents of the individu nate in this sur n às at to must their basis needs. pent a

That is only Petroless Mensiones has put forward the fear property to increase agricultural productivity by means of a vector atlantics of assessments and fordilars is agriculture, does increasing the increase of the agricultural actor, increasing to increase of the agricultural actor, increasing to increase of the agriculagricultural sector into the population economically active and establishing a sound basis for the further integrated growth of the whole economy of Mexico.

### 5. Conchisions

All that has been shown previously in the comments and in the tables points to an immediate and evident conclusion

It is necessary for Petróleos Mexicanos, the biggest industrial corporation in the country, to take a forceful stand on this major problem of Mexico.

The more immediate and forceful contribution of Petróleos Mexicanos to the solution of this problem is to make available to the agricultural sector ammonia and natrogenous fertilizers at considerably lower prices than at present. This can be achieved by the construction of large tonnage ammonia and urea plants, namely 1,000 tons per day of ammonia and 300 tons per day of urea. As plant capacity increases, operating costs decrease, thus Permex can make this large contribution to the welfare of the agricultural sector without impairing its financial position, since the proposed reductions in price of fertilizers will come from the reductions in operating costs obtained in very large capacity plants.

### B. Agricultural productivity

### 1 The violds of a few crops

(a) Cotton. The yield of cotton has increased from 250 kilos/hostare in 1960 to 652 kilos/hostare in 1963, this indicates that this part of the agricultural sector is the one in which technology is more widely used and is the one that has more resources at its disposal. However, it is estimated that in optimum conditions the yield of cotton in Mexico should be of the order of 850-950 kilos/hostare

(b) Caffee. In the period of 1925-1929, the visit of colles was 907 kilos/hostare, in the poriod of 1930-1936 the yield was 403 kilos/hostare, in the poriod 1961-1966 the yield was 419 biles/heatare, in 1945-1949 the yield was 407 kilos/hostare, is the period 1955-1959, 390 kilo/ hostare. This clearly brings out the point that the yield of colles have been decreasing through the years. The main reason for this is that coffee has been produced for years without adequate fortilization of the suil and thus the food electronic in the soil are being gradually numbed, with a consequent decremen in yis n. It in esterenting to point out fint the yields in 1962 were ne/hostore. This is due mainly to the wi tor uno of foreiti nore that year in which Pennen began the anis of furtilizers. Survey per coust of the product na af celles is experted and this part of the optimizant easter has collisiont recovers at its dispessit to promote feture expansion. The optimizant yield for cellus in bitation is of the order of 780-750 bitaglastant.

(r) Super sere. This part of the agricultural sector, which is one observe modern mathemic of polyactagy can be most easily employed, has shown instantificant increases in yields. These increases have been of the order of 0.7 per cent per year, despite the fact of the great demand for this product. At present the yield of sugar cane in Mexico is about 55,700 kilos/hectare, it is estimated that the minimum yield, using modern agricultural technology, should be 60,000 kilos/hectare. This implies a wider use of fortilizers, especially nitrogen

(d) Beans This agricultural food product is one of the bases of the diet of the Mexican population. Although this plant is able to fix nitrogen from the air, it is very important to apply fertilizers to the soil. The yields in Mexico at present are of the order of 380 kilos/hectare. Estimated yields in optimum conditions should be about 500 kilos/hectare.

(e) Corn. This is the most important food product for the country, considering that the consumption per capita per year in Mexico is 170 kilos, and this could be increased up to 190 kilos. Due to this fact corn is the base of the Mexican agriculture, as it generates by itself approximately 31.30 per cent of the total value of the agricultural production. Efforts are being made by several government institutions like the National Seed Commission for seed improvement However, the yield at present in Mexico is of about 100 kilos/hectare, and in some cases it reaches 900 kilos/hectare. It is estimated that the maximum yields of corn in Mexico, with fertilizer application, should be of the order of 2,000 kilos/hectare

(f) Where This product is the one that has shown the graniest yield increase in the last few years, due to the intensive application of fertilizers. The yield of when in 1950 was 950 kilos/hectare, and this yield grew to 1,956 kilos/hectare, in 1962 However, it is estimated that the optimum yield in Mexico should be of the order of 2,360-2,700 kilos/hectare, with the optimum application of fertilizers.

As can be charved, logical generalizations can be made on each agricultural erop in Mexico and the obvious conclusion is that the wider use of fertilizers, mainly nitrogen, should be given the leghost priority to achieve greater agricultural productivity in Menico

2. General situation of the solls in Mexico (those devoted to agricultural production)

(a) Description of irrigated land. The following routin have been found for the total areas susceptible to irrigation Total area being irrigated at present 4,454,354 hostares. However, when considering thes area, the following classification should be made

Norman and Statement

- (ii) Anoth of semared irrigation, included within the progation distribute of receiving the banadite of underground waters 3,378,384

Perns Addi.300

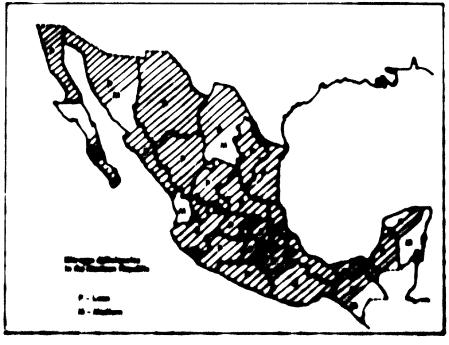
Of this invigoted land, it is estimated that the cultivated some resulted a total of 1,98,780 bastares, which was sufficiented in the following sussar:

(ii) Grains						Restores
Distant						555
Rice .						25,814
Calles .		· •			•••	150 1.484
Barley .						633
Deans						24,859
Chishpen .	•••	-				18,900
Bread bean a Corn	nd link	<b>.</b>	• •			2,500 356,047
Sorghum .				ана. С		1,900
Wheat						
						1.044.500
(iii) Other food pro	daata					1,000,000
Tomate					4	15,500
Chill						6,000
Verious.		• •				7,500
						2.00
(III) Pedder						-,
Aihih						21,000
Other .						3,000
						31,000
(br) Olaghana sand		• •	•••		• • • •	22,000
(v) Contan			• • •	<b>.</b>		775,000
(vil) Prutte						
(vii) Industrial plants						
(Begar cana) .		• •		· • ·		41,680
(vill) Planure .			. ,			200
				_		
					D TOTAL	1,000,700

(b) Non irrigated lands. The cultivated non-irrigated areas in Mexico power 11,641,220 hostares. This area is cultivated as follows:

200,000
-
585,689
121,000
264,000
200,000
239,689
1,340,000
6,372,000
948,089
1,130,000
11,377,000
264,000
1,041,239

(c) A on of the solly in Mex R. *P* I). In order to property as ns the agri nery, and show all of the for r of the cou d. a survey was made of the soil analysis of d us the aut try so as to dote s in the co أد أدد as far as four factors or variables which affect agrics tivity are concerned. These are: organic a . rephores and potassium. reges, ph



State	No of municipalities	Organic menter	Maragun
Agusseallantes	,	Poor	Peor
Territory of Bajs. California	3	Poor	Poor-Medium
Reja California State	1	Poor	Poer
Campada	3	Rich	Poor
Chiepes	4	Madium	Poor-Madium
Chihushus	Å	Peer	Phar
Contraits	Ĩ	Paur	Poor-Madium
Colima	ĩ	Peer-Rich	Poor-Madium
Districts fadaral	ź	Paer	
Destance		Paer	Poer
Guanaluato		Poor	Poer
Guerrero	J	Poor-Medium	Poer
Hidnigo			Poer
		Poor	Poer
		Poor	Poor
Michensin .	3	Poor-Rich	Poer
Moreleo	,	Medium	Peer
Nemerit	4	Medium	Poor
Nurve Lann	•	Medium	Medium
	3	Poor	Peer
	4	Peor	Peer
	4	Madium	Pour
	3	Peer	Poer
California Rev	1	Medium	Medium
en Lab Potasi	3	Pene-medium	Poer
linehe.	3	Peer	Pour
the second second second second second second second second second second second second second second second se	4	Poor	Pour-mailtum
	3	Peer-rish	Paar
inneulipee	3	Peer	Paar
Paneata a	3	Paur	Paur
Antones .	7	Page-risk	Paur
Panatan di Angela di Angela di Angela di Angela di Angela di Angela di Angela di Angela di Angela di Angela di	j	Paur	Paur
	i i	Paur	Paur

# (i) The soil analysis in Mexico is an follows

The above nomencluture is based on the following considuration

Poor self	•1
Madham and.	2-3
Rink and	+3

Per .......

Press this data we conclude that the general self situation in Manico is poor, expectably as for an altragen and expanic matter are concerned. Where expanic matter is concerned, the soils in Manico present the characteristics of an enhanced -oil and therefore it is not pecalitie to consider an efficient repeation by the syste of earliest and of the phone since there is not collision expanic matter in the soil and there will not be caught bartoria, thus the soil will not here many to replace nitregen. This is shown charaly in map No. 1.

### (iii) Aninfull conditions

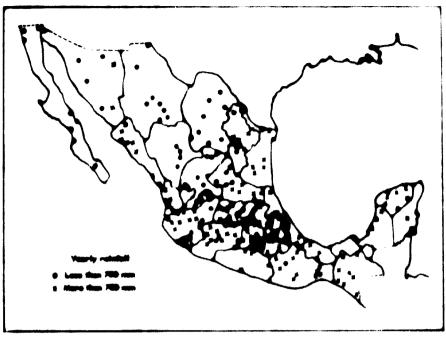
It has been determined in a conventional manner that the amount of veter required in an agricultural cycle is of the order of 700 mm. of related per year. This is in order to recognish the investments much, based on a minimum agricultural productivity. Based on the assurgtion, map No. 2 has been prepared, indicating in a cheer form the areas that have rainfulls larger or lower then 700 mm. per year. It is important to mention that although in general terms the monthly rainfull varies from area to area, the most common season is from May to Outplur.

### (iii) Domand of phosphorus and potassium

As you might see in maps Nos. 3 and 4, the need of phosphorus and potentium is not as oritical as that of mitrogen, since the rate of enhancement has been loss, and therefore we still find ponce with a medium or rich context of phosphorus and potentium.

This does not mean that we can discount the use of phengheres and petersium to carry on the present programme to insteam agricultural production; an the entitiery, three are important character to this purpose, but the attount accessary will be only that for each periouslar even, and we do not have to think in series of the attount independents to restore them to an entropyed cell.

Since we do not consider these elements of priceelements origin, we only point out that furtilizer plants, using antipulous summaris to produce granular furtlines, are considering this problem, and are producing complete furtilizers including the three counted elements:

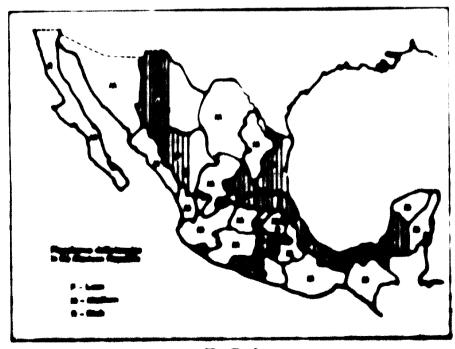


Map No. 1

altregen, phosphorus and potassium, in the proper amount for each cros.

(d) Rate of soll diplotten in Montes (with corresp agricultural product by by the comound of attragen without repeation). Is order to estimate the rate of diplotten of attragen is the solls of Montes, the following basis were used. (i) It is estimated that the reposition of altrages by basterial action, starting from organic matter, is negligible.

(ii) The amount of altregen contained in grain, strew etc. was estimated from chamber analysis. This altregen (with few encaptions) comes from the stearption by the plant of the altregen contained in the coll.







Therefore, if we consider on the one side the amount replaced in the soil, the difference of these two will give of attragen contents of the agreeultural production (by us a good idea of the rate at which nitrogen in the soil analysis), and on the other side, the amount of astrogen is being enhausted in Mexico.

	Norvasiai aras n Assarva tertara	Mald in Mile/Nectore	Patal production to demostat rate (980	Nitragen renewad in kolen graduer	Posti ampany of Allropen renerved in Intelyett
Products					
Rapaso Adhab Cathan Nao Ras Pranato	200	995	120		1,884
		44,685	4,715	•	28,290
	1,1 <b>30</b> 139	912 2,079	979 277	104	60,216
Cinta .	197		48 1	22 30	6, <b>89</b> 4 2,700
Pegande	74	1,397	H	3.1	310
	<b>10</b>	363	H	26	340
Collin	394		135	15	2,085
Rager appo	300 375	97, <b>395</b>	20,154	4.74	95,000
-		746 710	206 10	30 4	6,1 <b>50</b> 72
Gross diff		2,473			720
Diy ent Graen dell Dans Stad Temps Con. Petato Planaph. Vigeragh. Suglam	1.400	378	<b>799</b>		
Name I	140	773	120	8	998
Tungio	305	5,607	1,846	3.1	5,730
Com.	4,000 80		5,700	<b>9</b>	200,000
Parameter .		5,012 25,207	401	4.3 10	1,725
Watervieten		7,100	137	5	4,640 1,740
Saughum .	130	1, <b>30</b> 6	170	-	
		1,300	**	28.6	1,000
Wheel		1,398	1,405	27.9	48,399
College geochasts		792	206	28	7,390
Turns	13,300				<b>596,970</b>
	•	18,300			1,900
Parat	9	15,000		15	940
Adma.	16	6,000		20	1,000
		17,300	130		1,700
		H4,000	46 47	15	900
		16,500 16,600		<b>20</b> 15	1,340 7,005
	H	6.)86		17 28	1,005 1,075
Citizen	110	6,600	147	13	11,500
<b>.</b>		- •			-
TRINK.	272				30,045
Charle TOTAL	13,005				<b>907,88</b> 3

Thursdays, con ent of 507,883 tons per parting the a peer of altragen compared in 1960 and 195,000 of qualitatic altragen and 36,0 and calment facilitates, the difference but or the rate of enhancements of the soil in his

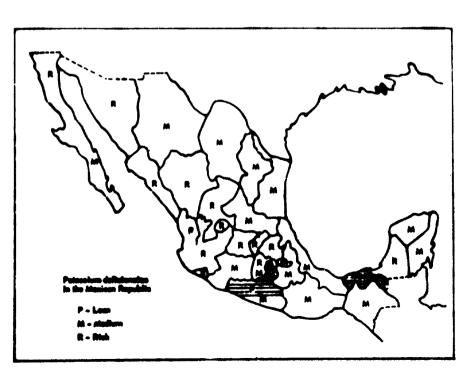
SHAD tons of allowing annuous per year 100,000 tons of changes replaced per year Allen and allenges adjacent par page

It is important to counder that this de 1 **Č**o erenge annual pickie and consider 10 C . n 🍝 ----

ng the emergent of 507,823 tens per reveal in 1900 and the amount of allengen and 38,600 tens of gran the difference between these gives then of the cell in Menlee, thus: 

(a) Minagan required in conditions of optimum agricul-need productivity. In order to estimate the searcest of altragen required in conditions of optimum agricultural productivity, the searce under cultivation, the type of erap cultivated and the recommended optimum curvates of altragen for each erap, were considered; thus the following results was obtained:

Products	fallingst one langes	Allowed and a second second	Tradi colonili d' desaran registret (1986)
(iii) Instantod lando			
Gratin.	1,011,500		88,500
Past products	39,000	ä	1,390
Fuller	31,000		3,100
Classicous seed	38,000		1,100
Cetten	173,000		15,440
Sugar sums	47,000	130	6, 199
Prulin .	8,000		4,000
Person	380	9	
Turns	1,985,789		198,489
(ii) Nan-irrigated lands			
	300,450 60,450 500,450	30	4,000
Regards Albelto Catton		100	6,000 10,000
Callon	500,000	*	
	101,000		6,010 1,040
	201,000	36	
luger ente		130	36,000 19,120
	299,000 1,349,000	<b>40</b> 14	14,500
Renno a la companya da la companya	6,373,680		346,000
	848,689		71,500
	1,130,000	3	36,389
Тота	L 11,377, <b>580</b>		
ditte Bander	264.000 ha	naraa < 30 bilaa/h.	- 7, <b>900</b> tuns



Map No. 4

(f) (urrent situation of the marker for nitrogen. The statistics of imports are given holow.

## (1) Imports of stirageness fortilizers

	Wiregonous (cretilisers	Por maine
	5 <b>6710</b> ,	1000
1990	13.415	1.185
1951	<b>10,770</b>	7.095
1952	23,070	13,609
1953	15,705	11.596
1954	10,221	16.995
1955	86,688	65.738
1956	117,135	\$3,328
1957	99,649	81.505
1958	112,300	FE1.303
1999	141,349	97.463
1960.	145,504	105.378

(ii) Mirragen equivalent of the imported fortilizers

	Mitragan - Iams	Palae in million peres
1950.	7,848	30 7
1991	9,296	19.8
1992	0,703	16.5
1953	10,300	11.2
1954.	19,460	13.2
1955	45,044	85.9
1956.	56,006	125.7
1997	97.896	106.9
1958.	76,300	126.1
1999	78,954	142.2
1960.	121,100	187.9

### (iii) Personning methods

Straightlinud trand of the historie ceries 1988-1989 and series 1954-1989, with straightlined entrapolation for the method of the minimum squares, thus:

Period 1952-1968

Ten of nitrogen = 14,397 + 13,827 × Betimation:

1965									193,900
1970									263,093

Period 1954-1960

Ton of nitrogen = 31,000 + 17,000 × Balimation:

											Patte
1963											218,809
1970										,	304,209

Therefore, the most optimistic forecast is the one of 218,009 tons for 1965 and 304,209 tons for 1970, and as was shown before, the real domand in function of the optimum productivity is of the order of 1,000,000 tons par year.

# (iv) Demand of agricultural production

(a) Composition and future domand of agricultural products. Considering that the average per capits consumption in considered the same as it was in 1962, the following will result:

	m	e di	NH.	r					Ello/tshabbast	Regulations 1943	nte in Sone 1970
Secame									3.8	149,693	173.539
Alfalfa			•						123.5	4.865.035	5,639,998
Cotton	•	•							4.9	157,572	182.672
Rice .									6.5	256,054	296,842
Oats .	•			•					2.5	96,482	114,170
Peanuta	۱.						•		2.2	86,664	108,470
Cacao	•	•	•	•	•	•	•	•	0.5	19,696	22,835

Product A	illia Antonioisee	Rogair country in constant
Sugar care	39.0	1 142 197 1 126 179
Barley	6.0	236,350 274,000
Dey ohele	84	15,757 18,261
Green shell	2 +	WI.004 (415.677
<b>Dans</b>	18.2	716.951 831.19
Steel	1 1	41.210 59 int
famato	# 2	123,02 4 174,479
(ann	166.0	6.488.452 3 484 552
Palate	85	394,8489 108 178
Phone pla	5.0	196, 464 228 198
Www.mpice	12	126,058 146 14
Yonghum	71	279,040 124,241
Falagoo	21	82,725 45 489
Wheel	MB (d)	1 406,914 1 715 184
Caller	1.5	19 (190) MI 102

the increases in the domainal for agricultural products as a result of the increased purchasing power of the agricultural vector. It we consider that agricultural productivity is increased by one hundred per cant over the present level, this mercase will have the fullowing results.

Fotol gross national product at current	1946.5	- <b>17 1</b> 97
prices	196,689	244,000
Orons national product of the agricul- tural assist at ourrant prices	16, ( <b>188</b> )	42,688
Contribution in persontage of the agri- outtural sector in the total gross national product	18.3 %	17 2 "
By understating the indices, we will have, with the base 1960 - 199	227 8	265 8

This increase in the total grass national product and in the agricultural sector as well, will give a yearly purchasing power per inhabitant, as follows.

	•
1965	1,510.00
1970	1,613.47

Whish in daily average are the following:

	•
1965	4.10
1970	
17/1	4.42

This will mean an increase in the consumption of basis food of the order of 2.1 for 60 per cent of the population, which will mean the following requirements.

Products	Kilo/cagina	Requirements 1965	
Rice	8.25	324,992	376,761
	5.0	196,965	228.340
	3.2	126,058	146.137
Sugar cans	36.8	1,449,662	1.680.582
	1.9	74,846	\$6,769
Burley	7.6	299,386	347,077
Beans	23.1	909,978	1.054.930
Temeto	10.4	409,687	474.947
	206.0	8,193,744	9,498,944
	10.8	425,444	493,214
Sorghum	9.0	334,537	411.012
	27	106,361	123,303
Wheat	48.0	1,890,864	2,192,064

(c) Conclusions. Comparing this data with the agricultural productivity in 1962 and considering the agricultural expansion programmes which will take place after 1970, the following situation will be reached in the balance of the domand and supply of agricultural products:

	Ganatia					
Products	4 100		1999 A 1989	1966 A. 1986	r <b>anta</b> A name	
	120	199	173	11		91 i
Allaith	4,715	4,885	3,689	199	984	<b>10.5</b>
Cotton	<b>919</b>	197	HOE			
Conten Neo Opin Presente	397	206	396		19	17.5
	11		114	6	12	24.5
Peacet	100		H			
	10	10		1	4	36.0
Cullo	130	99				
Super case	30, i 94	1,148	1,380			
<b>Burkey</b>	300	386	274	Я	-	94.7
Bry shill	10	15	N			
Quantum edititi		-	105	10		364
	500	796	801	197	172	<b>10</b> 9
	120	91	<b>99</b>			
Green dill Denn. Shui Transte	1,000	300	374			
	5,700	6,460	7,489		1,700	1,040.0
Putpto	401	304	305			
Planaggin	298	196	200		_	• •
Wetermeter	137	125	146		•	5.4
Bunghum	170	279	384	H	190	100.9
Telepone			96	••	13	4.9
Vieneraten Berghann Talanar Viener	1,405	1, <b>486</b>	1,730	34	270	205.4
	FUTAL					2,714.8

Thus, it is obvious that a great dual of the gain achieved in industrialization will be lest if agricultural production is not increased and agricultural efficiency is not improved, ence in the yage 1970 Manio will because a net improver of fixed of aggressirapidly 28,714,800,600.00 in order to fixed its instreasing papellation. Should this happen, there will certainly be a serious consensicritic cented by the large foreign containing requirements necessary to agget the fixed import bill.

At this point it is interesting to note the basic used to establish an equilibrium between the development programmes of the agricultural sector and these of the industrial sector. IV IMPORTANCE OF NYTHOUGH PRODUCTS FOR THE METROVENINT OF THE ADDICULTURAL SECTOR OF MERICO

A. Increases in agricultural productivity forenant with the wider use of nitrogen at reduced prices. The first stage of this forecast is to increase agricultural production to most the deficits shown in the last table of the previous chapter. This will result in the following:

		Plant A	a hilaihaanne	Total production		
Products	Cultivated Instance	Present 1960	Paran 1964	Th. Max Printin 1966	Ph. Anna Annar 1940	
<b>leanno</b>	238,000	503	750	120	146	
	101,000	46,005	<b>66,000</b>	4,715	6,001	
	133,000	2,079	3,500	277	400	
Dets	107,000	856	1,500	92	361	
	58,000	363	750	18	1	
	275,000	745	1,500	205	411	
Green chili	30,000	2.673	3,700		111	
	1,400,000	378	750	559	1.17	
Cern	6,900,000	836	2,500	5,700	17.45	
Watermelon	19,000	7,182	9,000	137	171	
	130,000	1,304	2,500	170	325	
	60,000	1,364	2,500	82	15	
	928.000	1,592	2,300	1,465	2,30	
Wheat	780,000	1,376	ay.300	1,440		

With the first stage implemented, the problem of consumption and supply of agricultural products will be met by Mexican production. B. The second steps will be to increase the production of these crops which are likely to have an expert domand. This forecast of their production is as follows:

	Culture	Plainte in	little rise conv		Post production				
	hannares	H	1474	Alto (antaro - Filipid	40 / eggs / / 949				
Cotton	1,130,000	912	790	179					
Calles	314,000	400	100	135					
Name and	300,000	97,586	45,000	38,154	4.79				
	148,000	773	L, <b>300</b>	120					
Tampie	395,800	5,687	7,580	F.846	3,497				

C. The shird stage will cover the increase in the production of the rost of the products. The forecast of this production is as follows

	Culture	Plankle in	hile/leaser	Point s	Paddardag
	<b>Aprilia</b> tes	His	1919	nik. Name ( Minist	·**,557*
Curle	6,500	2,690	3, <b>800</b>	17	26
Rodand	3, 100		1,800	2.7	5.6
	8,480	750	2,500	6.3	24
Passas	75,000	1,200	3,500		100
Breat palato	17,000	6,500	8,500	110	144
Battert auftres	56,650	1,400	2,500	81	146
Onion	16,000	4,580	6,580	72	109
	10,400	1,400	2,500	15	27
Dry chill.	24,380	730	1,000	H	44
Stringhome	5,000	1,500	1,500	8	12
Shentery	5,200	4,800	5.000	25	30
Chistern	146,200	888	1, <b>89</b> 0	110	274
Bread bases	41,500	788	1, <b>800</b>	32	76
Catter beam	12,000	780	1,500		10
	24,000	788	1,500	16	36
Cantaloupo.	13,300	5,700	7,900	76	101
Poteso	56,000	6,500	8,000	325	
Pinespin.	8,000	23,500	25,500	205	224
<b>1</b>	10,500	1,390	2,500	14	26
	8,070	12,000	15,500	101	134
Phone and a second	5,150	7,890	5,000		46
Constant and copys	75,000	•	•	234	315
	4,000	12,890	17,000	63	84
Gas	4,360	12,400	16,500	77	105
	14,489	7,200	9,500	103	136
Manay	1,490	28,300	25,000	29	36
Mange	7,990	18,900	23,000	150	183
Manhollo	1,300	14,800	16,000	10	23
Apple and grave					
	6,300	11,200	15,000	70	95
	63,500	10,550	15,000	<b>60</b> 1	982
Bunana	25,800	10,300	15,000	265	307
Reates bases	25,500	11,500	14,000	203	357
	12,000	5,900	6,300	71	78
Paper	1,800	20,000	25,000	36	45

· Coronat trees in production

D. Increases in the average purchasing power of the agricultural sector by the increase in agricultural productivity. From the tables above, in which the increases in agricultural productivity are shown, the gross national product can be estimated for the agricultural sector and its influence on the total gross national product, at prices of 1960, obtaining the following results:

### 1 Total grees national product

	:905	jänä	reno	iden
	-tatiotical	darappe in appic	reconciliant	Normane in ageie
	-rand	produce	reconcil	produce
Potal gross national product at 1980 potas (million of pasco)	E71, <b>500</b>	175.012	201.100	210,212

### 2. Gross national product of the agricultural sector

	1968 statistical recal	i Dåd Maradar in agric aradarr	rankana tanahana tanah	
Greas national product of agricul- tural spater in 1980 prices (mil- lian paseo)	16,7 <b>60</b>	21,012	16,500	38,348

### 3. Average purchasing power in the agricultural sector

	i <b>TOŠ</b> Statistati Irotal	i908 Moreau In agric. gradier		internation (p. carito. product
Parohasing power in the agricultural sector par inhabitant par year in 1960 prices	780.7	<b>80 i</b> . 7	710.7	<b>900</b> .7

4. Economic factors affected under forecasts as the population of the rural and farming sector is incorporated into the economically active population

(a) It is expected that if this programme is implemented for 1975 the value of agricultural production at current prices will be of the order of \$38,500 million peace, thus giving average purchasing power of \$1,200.00 peace per year and per capita.

(b) With the increases forecast, it must be considered that the local markets will increase with the creation of new demand. This will bring about greater investments in industrial installations and services that will obviously absorb a greater proportion of the population and thus diminish the population in the agricultural sector, and

¢.

in this way make more noticeable the effect of the increase in living standards of the rural and agricultural sector.

(c) Further steps will be taken towards the integration of the development of the country as new internal capital is generated that will be available for future investments without foreign finance.

(d) As the purchasing power of the agricultural sector is increased, this sector will have enough funds and resources to meet its pressing needs and more, thus contributing to the political stability of the country.

(c) As this programme is implemented, the fixed assets and money in circulation in the country will increase, thus creating a further demand for all types of goods and services.

# C. Plastic materials

# INTRODUCTORY SUMMARY

This part of chapter IV contains the papers given under this boading at the Conference. These papers describe various plastics and their growth in developing countries with special reference to their application in these countries.

Pinetics and synthetic resins represent one of the most dynamic sectors of the petrochemical industry. The wide range of plastic materials that exist today, their versatility and low cost, the large number of ways in which they can be formulated and the almost mexhaustible supply of raw materials, have contributed to the growing domand for them throughout the world.

At present the production and consumption of plantics have surpassed that of basis non-forrous metals such as zinc, copper and alum insum, and as a group they represent the biggest outlet of the petrochemical industry after netrogenous fertilizers.

In the developing countries plustics have already found a large number of enduses, particularly in the form of consumer gonds, and they have also been used in conjunction with other materials in such areas as the building industry and in packaging.

In most cases the plastic processing industries of the developing countries need to import the petroleum-based resins they use as raw materials from the more industrialized countries, and this involves the expenditure of important amounts of foreign enchange. As a result, some important industrial and construction applications of plastics have not yet been developed in these countries.

The papers presented herein deal with the possibility of establishing a petrochemical-based plastic resins industry in developing countries; the utilization of new materials and processes that may be suitable for adaptation to local conditions; the discovery of new outlets for plastic materials that can be of special interest to developing countries and the problems that these countries may find during the industrialization process.

# 1. PLASTIC MATERIALS

# Prepared for the United Nations Centre for Industrial Development by l'Institut français du pétrole

### Intermediate and and-products or second generation potrochemicals

The intermediate products are manufactured from the basic products and are at the start of the production of end-products.

In the following pages we shall be concerned with their production according to the breakdown of demand categories in the following major end-product lines consuming petrochemical intermediates: plastics, synthetic fibres, synthetic rubber, detergents and fertilizers.

### PLASTICS

According to chemical category the best performers, in terms of capacity of production and growth rate, are distributed as follows:

Polyolefins: polyethylene; Vinyls: polyvinyl chloride; Polystyrenes.

### POLYOLEFINS: POLYETHYLENE PRODUCTION

### A. Introduction

Nobody really knows the future of polypropylene and some plastic sales representatives feel polypropylene will be a big selling plastic, taking a good part of lowpressure process polyethylene's market. Others say that it is not exciting, pointing to some of its weaker properties. What is sure is that the polypropylene is taking longer to develop than originally expected.

On the other hand, polyethylene remains the top plastic in the United States. In Europe, it will be as successful as it has been in the United States and, in spite of PVC competition, it is felt that polyethylene will easily pass polyvinyl chloride in the next five or six years to become the first of plastics.

# B. Polyethylene production and consumption

According to its manufacturing processes polyethylene is usually divided into high-pressure (or low-density) polyethylene and low-pressure (or high-density) polyethylene. The first was discovered in the United Kingdom during 1933, and in 1939 full-scale commercial production ---- using the high-pressure process --- began; the last, needing low-pressure polymerization, was prepared in the

United States and in the Federal Republic of Germany during 1950; the polymer produced in this way has higher density and is more rigid than the former.

The United States is by far the largest producer, followed by the United Kingdom, the Federal Republic of Germany, Japan and France.

### PRODUCTION IN 196

### (in tons)

	High-pressure	Low-pressure	Total
United States	167,000	<b>19,0</b> 00	1,0 <b>20,0</b> 00 1 <b>86,0</b> 00
Federal Republic of Ger- many			1 <b>65,000</b> 65,000

The average annual growth rate of production from 1959 through 1963 was 27 per cent in the United States, 31 per cent in the Federal Republic of Germany and 38 per cent in France. Polyethylene is still a quick growing plastic in European countries where — except in the United Kingdom — it is well behind polyvinyl chloride; therefore capacities are increased in every country. World output forecast for 1965 accounts for 2,000,000 tons of polyethylene low-density and 830,000 tons of high-density, in 1970 output polyethylene low-density would reach 3,500,000 tons.

United States polyethylene production has reached this high amount thanks to giant refinery capacities and an extensive network of transport pipelines providing ethylene at low cost price.

Both production and consumption of polyethylene are rising; growth is likely to continue in all outlets, mainly in packaging, bottles, sacks, despite PVC competition.

In 1962 consumption was approximately as follows:

																ĸ	has coluce
United States															•		4.2
United Kingdom	ι.									•				•	•		<b>2</b> .t
France																	
Federal Republic	: O	ſ	30	rm	an	y.	•	•	•	•	·	•	•	•	•	·	t.8

We have to note the low *per capita* consumption in the Federal Republic of Germany; it results from the great part of production to be exported -- about 35 per cent in 1962.

The main outlets and the applications of HP and LP polyethylene are described later in this paper where the plastics, and particularly polyethylene, are taken as an example of petrochemicals utilization, in order to convert these products into industrial and consumer goods.

# C. Manufacturing processes

### High-pressure process

# (a) Mass polymerization process (I.C.I.)

Ethylene containing 0.06 per cent of oxygen and free from acetylene (used as a free radical yielding catalyst) is compressed at about 1,500 atmospheres and heated to about 190°C. This mixture is fed to astainless steel reactor which operates isothermically. A conversion of 25 per cent is typical and reaction time is only a few seconds. I he effluent from the reactor goes to a separator in which unconverted ethylene is removed, cooled and recycled to the charge gas compressor.

Liquid polyethylene from the separator is water-white and very viscous; it is extruded in a form which can be quickly chilled and solidified such as a continuous ribbon. The molecular weight of polyethylene varies widely with operating pressure; at 1,500 atm. the molecular weight ranges from 6,000 to 12,000, at 3,000 atm. from 12,000 to 24,000. The incoming ethylene stream must be free from impurities (normally 99.5 per cent ethylene is required); the absence of acetylene is particularly important. The oxygen content of the incoming ethylene is reduced to 0.001 per cent in order to add the accurate amount of oxygen required as a polymerization catalyst.

# (b) Water-solvent polymerization process (Du Pont)

The major difference with the I.C.I. process results in the use of a diluent, whether a solvent or not (hydrocarbon and/or water) for better controlling the very exothermic reaction. Ethylene is first liquefied by compression and cooling. Benzene is then added as a solvent of the resulting polymer and allows improved control of the reaction. The pressure on this liquid mixture is then raised to between 800 and 1,500 atm. and the mixture is preheated before introduction into the stainless steel reactor. Simultaneously water containing oxygen as initiator is injected into the reactor during the course of reaction to maintain a constant catalyst concentration throughout the reaction.

Unreacted ethylene held in the reactor effluent is removed and recycled. The polymer has a molecular weight of 18,000 to 30,000.

### Low-pressure process

With the invention of metal-derived catalysts the polymerization of polyethylene was allowed to be carried out under low pressure. Three processes are used:

### (a) Process using Ziegler catalysis

The ethylene charge gas is freed from water, oxygen, sulfur and carbon dioxide (poisons of catalyst) prior to being introduced into the reactor.

In a vessel, aluminium triethyl (AlEt<sub>e</sub>) and titanium tetrachloride (TiCl<sub>e</sub>) are held in suspension in diesel oil, heptane or chlorobenzene. The actual polymerization may be carried out in the same or in a different vessel from that employed for catalyst preparation. Ethylene is then introduced into the reactor under a slight pressure. Cooling is supplied to remove the heat of the exothermic reaction. The usual operating conditions are a temperature of 50 to 75 °C and near atmospheric pressure. The polymer forms like a powder or granules which are insoluble at the operating conditions. After completion of the reaction, unreacted monomer is vented and recycled, the reaction mass is quenched with water or alcohol to remove any active metallic residue, then filtered or centrifuged and the solid polymer dried.

It has to be noted that other monomers, propylene for example, may be charged and polymerized in this reactor.

### (b) Phillips process

As for the preceding process, water vapour, oxygen, carbon monoxide and most compounds of sulfur, nitrogen and halogens are poisons for the Phillips catalyst and must be carefully removed. (Their concentration should be below 100 ppm.) Characteristics of the polymerization reaction are as follows:

- Catalyst: chromium oxide associated with at least one oxide of silica, alumina or zirconia. The supporting material is a silico-alumina composite.
- Operating temperatures: 65-200°C.

Operating prossure: 20-50 atm.

Reaction diluents are paraffins ( $C_b$  to  $C_{12}$ ) or cycloparaffins (cyclohexane).

The great deviation in operating temperature results from several methods applied in the use of catalyst:

In fixed-bed operation reaction temperatures vary from 130 to 180°C; we get low molecular weight (5,000-20,000) polyethylene.

TABLE 1. 20,000 TONS/YEAR POLYETHYLENE PRODUCTION BY HIGH-PRESSURF AND LOW-PRESSURE POLYMERIZATION PROCESSES

	High pressure	Low pressure
Investment * (\$ million).	12	14
Raw material: ethylene at 99.95		
tons/year	21,600	24,000
Utilities requirements		
Electricity (10 <sup>s</sup> kWh/year)	36.000	33.000
Steam (tons/year)	80.000	400.000
Cooling water (10 <sup>s</sup> m <sup>s</sup> /year)	4.000	2,500
Fuel (10 <sup>4</sup> kcal/year)	-	13,000
Catalyst and chemicals	\$400,000	\$595,000
Labour		
Men/shift	5	5
Men/day		

· Including control laboratories and paid-up royalties.

In shurry process (the catalyst is maintained in suspension in hydrocarbon) temperatures range from 89°C to 169°C and we get high molecular weight polymer (46,000 and higher).

The rosulting polymer solution is filtered or centrifuged to remove the catalyst residues and polymer is recovered from the solvent which is recycled. The catalyst productivity is high enough to justify discarding the catalyst

The catalysts developed by Philips polymerize many other oleftes, above all propylene, by modifying reaction temperatures and pressures.

### (c) Standard Otl of Indiana process

The catalysts contains molybdena oxide on alumina Operating conditions are

Temperature	399-269 (C
Pressure	H-98 atm

The polymorisation is carried out in the presence of a liquid moduum which serves both as a selvent for the reaction products and as a liquid for removing calorise provided by the polymerization. The oldin must be free from oxygen, carbon discusse and suffit compounds acetylene and carbon monoxide can be overated.

This process offers other catalysis containing nuclei oxide and cohait supported on charcoal

### D. Economics of polyethylene manufacture

The elements of the operating cost for a 20,000 cons, year polyethylene plant, erected in Europe and based, respectively on low pressure and high-pressure pressure, are given in table 1.

The manufacturing cost and the derived selling price of polyethylone produced by these different techniques are given in table 2. Ethylone feedblock is taken at the current price of \$110/ton or \$6.15.

### TABLE 2. 20,000 TONOVARE POLYDYWYLDNE PRODUCTION BY HIGH-PROBRING AND LOW-PROBRIDGE FOR YMRINEATION PROCEEDED

		Unite cont	N.P. Pa	lpressionation	I. P. Pole	weriedlice
	( Jada	e nue com	Annual quantity	lanangi cast 10° Siyang	Annual evantity	inned con 18 <sup>4</sup> Bryon
Variable charges						
Rew material: ethylone	Tens	110	21,600	2,300	24,000	2,648
Utilities						
Electricity	HP kWh	ł	36,000	<b>}60</b>	33,000	330
Steam	Tens	1.6	30,000	130	400,000	640
Cooling water	10° m*	6	4,000	24	2,500	15
Fuel	10 <sup>4</sup> koni	1.5			13,000	30
Catalyst and chemicals				480		595
Labour						
Salaries and wages Supervision at 25 per cent of salaries	Men/year	5,000	24	129	24	120
and wages				30		30
TOTAL VARIABLE CHARGE	8			3,442		4,390
Fixed charges						
Depreciation       At 12.5 per construction         Interest       At 3.5 per construction         Maintenance       At 2 per construction         General plant overhead       At 2 per construction         Taxes and insurance       At 1 per construction	ent of total invest at of process unit at of total invests	itanent 's and off-sites ment				
	TOTAL	PERIO CHARGE	I	2,760		3,210
	MANUF	ACTURING COST	,	6,282		7,600
Solling price						
Net cash flow at 20 per cent of total in	vertment			2,400		2,800
Depreciation provides				1,500		1,750
Net income after taxes				900		1,050
Net income before taxes at 50 per cent.				1,800		2,100
Manufacturing cost				6,202		7,600
Polyethylene sales				8,002		9,700
				400		435
Polyethylene selling price 3/ton				18.2		433

### WHERE PER YVEN YE CHE ENDED PREDER PREDE

### A. PVC production and communition

The first patents on the polymortaution of vinyl chloride data from 1933 and were taken by EG Farbon in Germany

This indicates the hogenning of the development of plastic materials which are at present the most important mutorials in the world, both by those consumption and by their production. It should be noted that the increase of PVC is grouter in France and more generally in the European countries than in the United States hotwoon 1994 and 1961 the avorage annual morouse of the production was about 26 per cont in France and 13 per cent in the United States. The market of plastic mutorials in Europe is dominated by PVC whereas in the United States there is providently an equilibrium hotwoon PVC polyothylene and polyotyrene This differ once is due to the origins of the chemical industry, which in Europe is based on charcoal, boing the raw material for the proparation of plusticizors and vinvi chloride starting from autiviene. Moreover, the American market is wide enough to permit the installation of plants for the production of onlylene which can reach the most competitive capacities.

In 1962 the consumption per capita in different countries was as follows

	ing/cagnes
Federal Republic of Germany	3.6
United States.	31
United Kingdom	27
Fanoe	2.6
italy	2.2
Benchex	2.0

The romanch started in order to develop the applioutions of PVC in huilding and particularly in agrioutime seems to ensure still turther the rise of the consumption of this plastic. As a consequence the expansion of the plasts have been increased or plasts producing PVC by new coutes have been constructed in the limited states. France foctural Republic of Ciermany Italy Einted Kingdom, Japan etc.

The applications of PVC are prevented in Chapter VI hereafter

### 8 Manufacturing processes

# (a) View Aloride production

There are two main routes to vinyl chloride and hence to PVC. One route is via the addition of hydrochloric acid to acetylene. The other route is via the chlorination of ethylene to give dishlorionthane, which can then he thermally decomposed to give vinyl chloride and HC.

As regards the inchangues of vinyl chloride production onch route has a disadvantage in the othylene coute half of the chlorine used appears as ACI which usually means that half the chlorine is effectively devalued. The acetylene route is a hydrochloric consumer but it is based on acetylene which as compared to ethylene is a high-cost chemical.

In the othylene route up till now the hydrochloric acid co-product has been an economic millistone around the othylene route's nock. There is far more co-product MC1 produced from the constron plants than there is a requirement for Electrolysis of the acid back to chlorine is only feasible if very cheap power is available and as a consequence the hydrochloric acid has often to be de-

### TABLE 3. 20,000 TONN/YEAR VINYL CHLORIDE PRODUCTION Elements of operating cost

	Ciae I Accepting reads	Case 2 Brighten route BCI co-product	Case 3 Acertphone and eduptone (redatorits	Case 4 Between rease No co-product B
Investment (\$ million):				
Press units and eff-sites.	2 •	2.5	3.1	4.0
Row materials balance (tons/year)				
Bilgimo		10,000	5.000	10,000
Acetylene	8,600		4,300	
Chlorine		25,400	12,700	13,400
	12,000	prod. 12,400		
Utilities requirements				
Electricity (10 <sup>s</sup> kWh/year)	5,800	5,800	5,800	7.329
Steam (tone/year)	3.400	46.000	24.800	73,000
Cooling water (10 <sup>e</sup> m <sup>2</sup> /year)	320	5,500	2,910	7,700
Process water (m²/year).		26,000	13,000	32,000
Fuel (10 <sup>e</sup> kcal/year)		16,000	8,000	16,880
Catalyst and chemicals (S/year)	15,000	16,000	16,000	50,000
Labour (men/shift).	5	5	1	7

\* This investment is based on purchased HC1. If HC1 is not available, manufacturing plant producing HC1 from abhorine and hydrogen must be included.

### Trates 4. 20,000 reserves Vervs. creasures standards Manufacturing ever and selfing autor

Case I. Accelerate results

-				
	6 August		tentinat and the	The second
Partable elutions				
New materials				
Analylana	Penn	395	8,000	3,040
	Pana	10	12,000	
Unillian				
Mantenaty Stans	H <b>P</b> HNN Form	NO 1.6	5,000 3,000	
Exating water	100	6		1
Presses water		0.2		
	HP had	19		
Catalyst and chemise's				<b>14</b>
Labour			-	
Referine and wegan Repervision at 25 per apat of	Nen/year	3,000	30	
salaries and wages				26
POVAL VARIABLE CONQUER				1.96
Pland sharper				
Representation	Ar 19	.5 ppr cent of	and and improved and the	
Interest	AL 3	J pur cast of	intel investment	
Maintenance General glass overlaged		per cast of		
Tenn and Insurance		per cent of per cent of		
		Topu	L FINED CHARGE	
		MARU	PACYUMING CODT	4,046
Not each flow at 20 per cent of total				
Depresiation provides Not income after tenes		• • • • •		290
Not income before tenes at 50 per ce	#			150 300
Hendesturing cost		· · · · · · · ·		4,046
Mind changes and a set				
Vinyl oblorido salos Vinyl oblorido solving prine S/ten		• • • • • • •		4,346
		· · · · · · · ·		217 9.9

stroyed by neutralization. The cost of the chlorine vernu the hydrochloric acid plus the cost of neutralization is a heavy charge against the vinyl chloride product.

### Hydrogen chloride consumer

First solution. For vinyl chloride production the most usual way of avoiding the hydrochloric acid problem has been to make use of the addition reaction of HC1 and acetylene to give vinyl chloride. This addition reaction can be used to balance the hydrochloric acid made from an ethylene-based plant, in which case there is no production or consumption of acid. However, the disadvantage of using acetylene instead of ethylene is its higher cost and this is to be balanced against the loss in the value of the chlorine caused by its degradation to HC1 in the ethylene route. Furthermore, as against this, two reactor systems are required, each with half the capacity of the total plant: this increases the manufacturing cost by raising the fixed charges per ton of vinyl chloride produced.

Second solution. To avoid the extra cost of feed separation, vinyl chloride can be produced from a mixed feed of acetylenc and ethylene directly from a naphtha pyrolysis plant. In this process, the vinyl chloride reactor is running in series instead of in parallel. However, this route still suffers from the need to use triple-bond acetylene for a product — vinyl chloride — which only contains a double bond.

Third solution. The HCl co-product is oxidized back to chlorine using a modified Descon process, and recycled

in the differentian step. The basic reason for the interest of this process is that

It uses others which costs half as much as austriana Only one reactor system is required instead of two in the "maned route"

The advantages of size can also be taken

## Economics of viewl chlands manufacture

The elements of operating over for a 20,000 tons/year onyl ableride plant based on the following cases are given in table 3

- ( are / Acotylene route
- Case 2 Bibylone mute on-product MC1 not valuemend
- Case 3 Austylene and othylene feed-stauks with two reactions in penallel (see hit solution for consuming HC1)

The manufacturing cost and the durited setting price corresponding to such a unit are presented respectively in tables 4.5.6 and 7 for the different cases haved on this typical accommic hypothesis.

Anna santeriation prives	8-7-10
Ethylana	1.10
Austylens	205
( Tolescone	
ME I covariable as by-presduat)	12
HE I must available and produced from obterme and	
hydrogen)	70
By-product HE I court valuesand).	
By-product HE I (valorised after conversion into	
objective by algestralyses)	12

# The following results can be obtained

Case 1	View character college proces
Austylana mute	Crami
MC1 is available as by-gendlast at \$32 */tan	200
HC'I is not everlable and is purchased at \$78 to	
tem	217

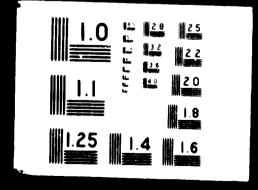
# Table 5. 30,000 Teles/Vene verif. Character resources

Case 2 . Rthylene route, HC1 se-product

	time	their cost B	Annual quantity	
Variable changes				
Rev materials				
Biliptone	Tem	110	10,000	1,100
Chierine	Tons	70	25,480	1,700
Re-product HC1.	Tons	•	(12,400)	-
Linking		_		
Neuroinity and a second second second second second second second second second second second second second se	₩ <sup>p</sup> kWh 'Yeese	10 1.6	5,000	59 73
Cooling water.		1. <b>.</b>	3.300	33
Protein weiter	1110	0.2	26,000	5
	19° keel	1.5	16,000	24
Catalyst and chamicals				16
Labour				
Salaries and wages	Man/your	5,800	20	100
salaries and weges.				25
TOTAL VARIABLE CRARGES				3,214
Ined charges (see table 4 for distribu	<b>tice)</b>			575
		MARI	PACTURING COST	3,789
Not each flow at 20 per cent of tota				500
Depreciation provides				310
Not income after taxes	••••		• • • • • • •	190 300
Manufacturing cost	•••••	 	· · · · · · · ·	3,789
Vinyi chioride sales				4,100
Visyi chloride selling price (\$/ton) .				206
				9:5

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# 6 OF 7 04573 -04574 VOL 1



# TABLE 6. 20,000 TONE/YEAR VINYL CHEORIDE PRODUCTION Manufacturing cost and selling price

	Untr	Unit cost S	Annual quantity	Annual cost (10° \$/year)
Variable charges			an ge-orden ger verstellen verste affere verste	
Raw materials				
Acetylene	Tons Tons Tons	295 110 70	4,300 5,000	1,270 550
Utilities	1012	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	12,700	890
Electricity	10 <sup>a</sup> kWh Tons 10 <sup>a</sup> m <sup>a</sup> m <sup>a</sup> 10 <sup>a</sup> kcal	10 1.6 6 0.2 1.5	5,800 24,800 2,910 3,000 8,000	58 40 17 7 12
Labour				16
Salaries and wages Supervision at 25 per cent of salaries and wages	Men/year	5,000	28	140 35
TOTAL VARIABLE CHARGES				3,035
Exed charges (see table 4 for distribut	ion)	•••••	•••••	720
		MANU	ACTURING COPT	3,755
Net cash flow at 20 per cent of tot Depreciation provides	• • • • • • • • •	•••••	• • • • • • • • •	620 365 235 470 3,755
valy caloride setting price (3/ton).		•••••		4,225 211 9.6

Case 3: Acetylene and ethylene parallel routes

Case 2: Ethylene route, with co-product HC1	Phot oblockle adding price (8/sm)
HCl is not valorized HCl is valorized for other production at \$32/ton	208 189
Case 3:	
Acetylene and ethylene parallel routes	211
Case 4:	
Bthylene route, no co-product HCI	202
• This price is based on the potential utilization of H	CI as chiering

ł

fued-stock; it is calculated as follows:

Chiering poles	
Chlorine price. Cost of chlorine manufacture starting from HCI	70
Boundary in an and the starting from HCI	38
By HCl synthesis from shiorins purchased at \$ 70/ton and h	

2

This comparison between the different routes and processes shows that it is not possible to make a definite choice. The selection of the route and the choice of the feed-stock to be used in each particular project involving vinyl chloride manufacture, will be made specifically taking into account the availability and the prices of the raw materials and the utilization and the prices of the by-products in the area concerned by such a project.

# (b) Vinyl chloride polymerization

# Polymerization in emulsion

This operation is processed continuously in an autoclave provided with a paddle-agitator and from which air is driven out by a stream of inert gas or vinyl chloride before the beginning of polymerization.

Water, catalysts, emulsifying agents and vinyl chloride are mixed in the polymerization reactor.

Water has to take off heat evolved by the very exothermic reaction and to keep the viscosity of the solution low enough to allow an easy stirring.

Catalysts soluble in water are: potassium persuifate, hydrogen peroxide or a redox system.

- Emulsifying agents include anionic surfactants like various sulfonated hydrocarbons or, more recently, non-ionic surfactants. They promote an intimate contact of vinyl chloride with catalyst.
- Protective colloids such as polyvinyl alcohols or cellulosic derivatives are used for latex stabilization.
- Unreacted monomer vinyl chloride is removed from the reaction products and recycled. The latex obtained is spray-dried.

# Suspension polymerization

This is a widely used batch process. Water, catalysts, protective colloids and vinyl chloride are charged into a reactor under pressure with an agitator device. The reactor is free of oxygen of air which is an inhibitor of polymerization, by a stream of inert gas or vinyl chloride.

Catalysts are organic peroxides not soluble in water (benzoic peroxides).

Protective colloids are polyvinyl alcohol or cellulosic derivatives.

After a 90 per cent conversion of monomer the reaction is considered as over; unreacted vinyl chloride is separated and recycled. Meanwhile, polymer in suspension may be washed with water; then it is centrifuged and completely dried in rotary dryers; polyvinyl chloride is obtained as a powder.

The main differences between these two processes result on the one hand in a higher operating cost for emulsion PVC, because of spray-dryers, and on the other hand in the qualities of emulsion and suspension PVC.

Emulsion polyvinyl chloride is used for preparing latex or dispersed in plasticizers for making plastisols.

# Economics of polyvinyl chloride manufacture

Elements of operating cost for a 20,000 tons/year PVC plant, based, respectively, on polymerization in suspension and polymerization in emulsion, are given in table 8. Manufacturing cost and derived selling price for such a plant are presented in table 9.

# TABLE 7. 20,000 TONE/YEAR VINYL CHEORIDE PRODUCTION Manufacturing cost and selling price

Case 4: Ethylene route, no co-product HC1

	Unit	Unit cost \$	Annual quantity	Annual cost (10° \$/year)
Variable charges				
Raw materials				
Bithylene	Tons Tons	110 70	10,000 13,400	1,100 940
Utilities			13,400	<b>940</b>
Electricity	10 <sup>s</sup> kWh Tons	10	7,320	73
Cooling water	10 <sup>6</sup> m <sup>2</sup>	1.6 6	73,000 7.700	117 46
Process water		0.2	32.000	7
Peel	10° keel	1.5	16,000	24 50
Labour				
Salaries and wages	Men/year	5 <b>,90</b> 0	28	140
salaries and wages				35
TOTAL VARIABLE CRARGES				2,532
land charges (see table 4 for distribu	Kios)		••••	920
		MANUT	ACTURNO COPT	3,452
Not each flow at 20 per cent of to				
Depresiation prevides		· · · · · · · ·	••••	809 500
Not income after tunes .			• • • • • • •	380
Net income before taxes at 50 per (	<b>NOT</b>			
Manufacturing cost			••••••	3,452
Vispi ebiorido anias				4.042
Vingt chierids colling price (l/ton)				

### POLYSTYRENE

### A. Polystyrene production and consumption

Polystyrene has not had as bright an entrance in the thermoplastics market as both PVC and polyethylene. its two major competitors. Polystyrene was discovered in 1845, but commercial interests for it began to be shown only in 1930, when better knowledge of the mechanism of styrene polymerization allowed the reaction to be successfully carried on. However, the first polystyrene articles were stricken with bad shortcomings; they quickly lost mechanical properties and good appearance, and as a result presented no usefulness. Once more, polystyrene was forgotten until the end of World War II, during which large plants manufacturing styrene monomer were constructed in order to meet the requirements involved by the synthetic rubber programme in the United States. The failures occurred in the first attempts to commercialize polystyrene resulted from a lack of purity in the styrene monomer but from 1946 large quantities of high purity styrene monomer were available at a moderate price and they made polystyrene

TABLE 8	B. 2	0,000	TOP	48/1	BAR	PVC	PRODUCTION
		Eleme	nis.	of	oper	ating	cost

	Polymerisation In suspension	Polymerisation in envision
Investment (\$ million) Raw material consumption: vinyl	2.3	2.9
chloride (lons/year)	21,600	21,6~0
Utilities requirements		
Electricity (10 <sup>a</sup> kWh/year)	8,200	9,000
Sleam (tons/year)	46,000	80,000
Cooling water (10 <sup>s</sup> m <sup>s</sup> /year)	1,800	2,000
Process water (m <sup>3</sup> /year)	80,000	200,000
Catalyst and chemicals		
expenses (S/year)	140,000	300,000
Labour (men/shift)	4	. 4

production start again. Other modifications improved polystyrene properties, leading to high-impact and heat-resistant types which gave satisfaction to the custo-

TABLE	9.	20,000	то	NB/YI	EAR	PVC	PR	ODUCI	TION
M	lan	ufacturi	ne	cost	and	l selli	w	price	

		F		in suspension	Polymerization in emulsion		
	Unit	\$	Annual quantity	Annual cost (10 <sup>4</sup> \$/year)	Annual quantity	Annual cos ( 10° \$/your	
Variable charges							
Raw materials : vinyl chloride monomer . Utilities	Tons	205	21,600	4,450	21,600	4,450	
Electricity	10 <sup>0</sup> kWh	10	8,200	82	9.000	90	
Steam	Tons	1.6	46,000	73	80.000	128	
Cooling water.	10 <sup>8</sup> m <sup>a</sup>	6	1,800	11	2,000	12	
Process water	mª	0.2	80,000	16	200,000	40	
Catalyst and chemicals				140	-	300	
Labour							
Salaries and wages	Men/year	<b>5,00</b> 0	16	80	16	80	
and wages				20		20	
TOTAL VARIABLE CHARGES				4,872		5,120	
Red charges (see table 4 for distribution) .	••••			530		670	
	MANUE	CTURING CONT		5,402		5,790	
Not cash flow at 20 per cent of total invest				460		580	
Depreciation provides				200		340	
Net income after taxes				170		220	
Net income before taxes at 50 per cent				340		440	
Manufacturing cost	• • • • • • •	• • • • • • •		5,402		5,790	
PVC sales				5,742		6.230	
PVC selling price (\$/ton)				387		311	
(or #/16)				13		14.2	

mers and warranted its development. Production and consumption were as follows:

	Production In 1963 (1084)	Commption In 1962 (Ale per Capita)
United States *	670,000	1.2
Federal Republic of Germany "	142,000	
United Kingdom *	77.000	0.98
Italy	67,000	-
France	53,000	1.07

 Styrene resins containing 50 per cent or more styrene (excluding acrylonitrile, butadiene styrene and styrene acrylonitrile).

<sup>b</sup> Polystyrene and polyviny! acetate.

" General purpose, high-impact and expandable polyslyrene.

### B. Polystyrene processing and applications

### (a) Polystyrene compounding and processing

The term polystyrene refers to a large range of resins having different compositions and distinctive properties as for end-products; as a result, polystyrene is known amongst several types:

- Unmodified polystyrene or standard polystyrene is a pure polystyrene and is the cheapest. This type represents about 50 per cent of the whole production of polystyrene.
- Impact polystyrene is a combination of polystyrene with rubber. Two ways are followed to obtain this combination:
  - By mechanical mixing (in a Banbury mixer, for example), a homogeneous blend of polystyrene and rubber is prepared. At the same time other ingredients — mainly colorants — may be added; the final blend is dropped from the mixer into an extruder in order to get pellets of polystyrene.
  - By dissolving rubber, usually a styrene-butadiene type, in a mixture of solvent and styrene; then this mixture is polymerized. A large part of the styrene polymerizes with itself, the other part adds or grafts on to the rubber chain, hence the name graft copolymers, sometimes given to these polymers.

Most impact polystyrenes today are graft copolymers.

- Heat-resistant polystyrene is a copolymer of styrene with methylstyrene.
- Styrene may be polymerized with other monomers as acrylonitrile-butadiene or acrylonitrile (copolymer styrene-acrylonitrile is sometimes known under the name of chemical-resistant polystyrene).
- Finally, polystyrene is more and more used in the form of foam materials prepared by two different manners:
  - The first is to inject a volatile liquid into molten polystyre and to keep this mixture under pressure until it is extruded into foam boards. The combination of polystyrene with volatile liquid is prepared just before use.
  - The second consists in forcing, under pressure, a given amount of volatile hydrocarbon into pellets of pure polystyrene. Pellets processed in this way

are called expandable beads, because the application of heat will cause the polystyrene beads to expand.

All these types of polystyrene resins are easily compounded with colorants; in practice plasticizers are never used with it and are extruded into pollets. At least 65 per cent of polystyrene consumption in the United States and United Kingdom is converted into endproducts by injection moulding, and this percentage must be the same in other countries. The remainder of polystyrene is converted by means of extrusion and thermoforming. Table 10 shows techniques for converting polystyrene and its end-uses.

# (b) Polystyrene applications

Usual polystyrene types have been pointed out previously; they have all nearly the same fundamental properties, derived from specific properties of pure polystyrene, one of them being deeply modified in the way expressed by the qualification heat-resistant, chemical resistant or high-impact, associated to polystyrene in order to meet the requirements involved by utilization of polystyrene consumer goods:

Polystyrene properties responsible for its uses are summarized as follows:

- Light weight; with a 1.03 specific gravity pure polystyrene is placed between PVC (1.4) and polyethylene.
- Good electrical properties which remain fairly constant despite varying temperature and frequencies. Dielectrical strength is lowered in high-impact polystyrene or styrene-acrylonitrile copolymers because of the presence of additives.
- Good resistance versus alkalies and weak acids, but polystyrene is attacked by oxidizing acids, and softened or dissolved in aromatic and chlorinated hydrocarbons, in ketones and oils. Styrene-acrylonitrile copolymers are indifferent to gasoline and edible oils and have better resistance against other solvents.
- Polystyrene is free of odour and taste, and is non-toxic.
- The colourless polystyrene is one among plastics having the best optical properties (used in light diffusers).
- From conversion considerations, polystyrene is easy to mould, particularly due to its excellent dimensional stability and it is very easily coloured.
- Polystyrene does not resist ultra-violet rays and as a consequence develops a yellowish straw-cast which impairs mechanical properties by making it brittle. This failure prevents external uses for polystyrene products.

Applications in packaging. In 1963, packaging represented about 13 per cent and 24 per cent of the polystyrene consumption, respectively, in the United States and United Kingdom. Polystyrene is mainly used in food packaging, in various forms such as disposable cups (used in picnic or in slot machines for hot and cold drinks), containers for ice cream, ready-to-eat dishes and jams, films as lids for previous containers.

Cigarette packing is a new application of polystyrene in this field. These packages are made with normal or more often with high-impact polystyrene by moulding or thermoforming sheets in numerous shapes. Films

	•	Injection moulding	Parts of refrigerators, freezers, washers and dryers, sir conditioners Parts of radio and television sets Light shields Wall tiles
			Houseware, toys, shoe heels
Polystyrene		Moulding of expandable polystyrene	Low-temperature insulating applications (refrigerators, freezers, air conditioners) Boxes for industrial and consumer packag- ing, containers Sandwich panels for construction uses Foam boards for insulating panels or insu- lations in building, uses in the field of buoyancy
	•	Extrusion	Oriented films Sheets for thermoforming Foam boards
		Thermoforming	Disposable packages Containers Inner lining of refrigerator doors
		Extrusion of expandable polystyrene	Films, sheets for lining or thermoforming
		Spread-coating	Paper and textile coating
	<b>,</b>	Latex	Floor polishes Paints and coatings

are biaxially oriented by extrusion, which means that plastic is stretched in two directions in order to improve mechanical properties of the film. Forecasts promise a great outlet for polystyrene as packaging material, the major advantage against other competitors in this market being low cost and attractive shapes and colours of these thin-wall containers.

Refrigerators, freezers, air conditioners, washers and dryers. Many different parts of a refrigerator or a freezer are fabricated from both normal and high-impact types of polystyrene, due to its good behaviour at low temperatures. In refrigerators, the largest part is the inner lining of the door, fabricated in high-impact polystyrene; other less important appliances are crisper trays, egg shelves, freezer doors, control knobs. Polystyrene is used to fabricate house fans and air vents and various parts of air conditioners. In washing machines, control panels are chiefly made of heat-resistant types of polystyrene.

Miscellaneous. Innumerable and various shaped articles are made with polystyrene. The most important of them are listed hereafter; each article considered separately does not take a great share in the whole consumption of polystyrene, but the total amounts, for 1963 in the United Kingdom, to about 40 per cent of it and probably this figure is the same in other countries converting polystyrene.

The injection-moulding process is well fitted for economically manufacturing these items which are mostly of small size and of complicated shapes; this is due to the high production rates and greater and greater automaticity which lowers labour charges.

Applications in electricity

Television and radio cabinets, completely or partly Battery caves

Tape recorder reels

Applications in building

Lighting shields

Signs

Tiles for covering walls in kitchens or bathrooms Houseware

### Toys

Foam polystyrene. Main applications of foam polystyrene are based on its outstanding insulation characteristics and mechanical properties. As said previously, foam polystyrene is available in expandable beads turned into end-products by injection moulding or into films, and foam boards of desired sizes by extrusion.

By injection moulding, foam polystyrene is used for making component parts for refrigerators, toys, novelties, disposable cups and boxes required for packaging industria' and consumer goods claiming protection against shock during shipment; for example, typewriters, electronic parts, precision equipment, glass ware.

One of the most interesting applications of foam polystyrene lies in panels formed by two sheets of plastics, plywood or aluminium, between which the expandable polystyrene is foamed. These panels are used in the construction industr; for interior or exterior walls and as thermal insulating boards for tanks, tank waggons. Films made of expandable polystyrene serve as liners and are laminated to high-impact polystyrene sheet or paper-board, after which they are thermoformed into package boxes.

### C. Styrene manufacturing processes

The production of styrene is carried out in two steps: The first deals with linking of ethylene and benzene to form ethylbenzene:

The second involves dehydrogenation of ethylbenzene into styrene.

### Ethylbenzene manufacture

(a) Aluminium chloride process

The basic reaction:

# $C_{e}H_{e} + CH_{1} = CH_{1} \rightarrow C_{e}H_{e}CH_{1}CH_{8}$

occurs in liquid phase at a temperature of about 95°C under slightly elevated pressure. A small quantity of ethyl chloride may be added as a promoter for the reaction. Ethylene and benzene feed-stock must be carefully dried and be of high purity: at least 99 per cent for benzene and about 95 per cent for ethylene Geneous ethylene is fed at the bottom of the reactor and flows upwards, thus providing a turbulence that promotes an intimate contact with benzene flowing downwards from the top of the reactor. Anhydrous aluminium chloride in solid form is also introduced at the top of the reactor.

The reactor effluent comprises ethylbenzene, di, tri, and higher components of ethylbenzene, unreacted benzene and a sludge layer containing almost all the catalyst. This catalyst is removed and a part is recycled in order to reduce aluminium chloride consumption. From the remaining mixture, ethylbenzene is separated in a series of distillation columns, while polyethylbenzene and unreacted benzene are recycled. The presence of aluminium chloride and ethyl chloride generates hydrogen chloride, and as a result, the reaction must be carried out in special construction materials (enamelled reactors, for example) resistant against corrosive atmosphere.

### (b) Alkar process

This is a fixed-bed alkylation process designed to produce ethylbenzene, even with a low-concentration ethylenc from by-product gas. The reaction principle is the same as mentioned in section (a) above.

### Ethylbenzen • dehydrogenation

According to the following reaction ethylbenzene is converted into styrene:

$$C_{q}H_{q}CH_{1}CH_{1} \rightarrow C_{q}H_{q}CH = CH_{1} + H_{1}$$

Optimum conditions of this strongly endothermic reaction involve low pressure and high temperature, about 600-650°C; it is carried out with a metal oxide catalyst. The reduction in pressure is achieved by the use of superheated steam which at the same time removes any carbon deposited on the catalyst.

The effluent gases from the reactor are condensed into a liquid containing benzene, toluene, styrene, ethylbenzene and tar. Removing of benzene and toluene is easily processed in a fractionating column, but separation of styrene and ethylbenzene proved to be difficult because of the small difference in boiling points and the trend of the styrene to polymerize. A solution has been found by adding sulfue as an inhibitor to the mixture styrenecthylbenzene and carrying out the distillation under vacuum in a two column system. Ethylbenzene is recycled; styrene produced has a purity of 99.5 per cent or better as required for polymerization.

### Economics of styrene manufacture

The elements of operating cost for a 10,000 tons/year plant are given below:

### Investment

Process units (\$ million).														2.2
Raw materials consumption	(	tor	18/	ye	ar)	)								
Ethylene (at 95 per cent w	rt i	mi	n.)											3,360
Benzene (nitration grade)				•		•	•				•			9,240
Utilitics														
Electricity (10 <sup>9</sup> kWh)														1,300
Steam (tons)														100,000
Cooling water (10 <sup>s</sup> m <sup>s</sup> ).				•					•		•			5,000
Process water (m <sup>3</sup> )	·	·	•	٠	٠	•	•	•	•		•	•		35,000
Fuel (10 <sup>4</sup> kcal).	٠	·	·	٠	·	•	•	•	·	•	•	•	·	27,000
Catalyst and chemicals (\$) .												•		50,000
Labour (men-shift)		•				•								6

Manufacturing cost and derived selling price for such a unit are presented in table 11.

### D. Polymerization

Mass polymerization. Pure styrene is fed into a kettle provided with a paddle-type agitator; peroxide catalyst may be added or not. Under atmospheric pressure and by heating, prepolymerization occurs until a highviscosity solution of polymer and monomer styrene is obtained. From this point, either unreacted monomer is separated from the polymer by vaporization, or — the most usual way — polymerization of the solution is processed nearly to completion at temperatures considerably higher than that used for polymerization. The product is milled and extruded into pellets.

Efforts have been made to convert this batch process into a continuous one; the general principle has been left unchanged, that is to say, polymerization starts with the preparation of a viscous solution in several kettles by heating at about 80°C. The solution containing about 40 per cent of polymer flows continuously into a tower which has temperatures ranging from 100°C at the top to 180°C at the bottom, where the polymerization is over. The polymer is removed and sent to an extruder for pulletizing. Equipment for this continuous process is important and there are mechanical problems in moving highly viscous finished polymer, but the molecular weight of this polystyrene is more uniform than that of the batchprocess polystyrene. This batch process is very versatile and gives any type of polystyrene.

Suspension polymerization. Styrene is fed into a packed autoclave and dispensed in water by stirring with the aid of organic or inorganic dispersants, such as polyvinyl alcohol or calcium phosphate. The polymer is obtained in the form of small pearls which are washed to remove dispersants, dried and then converted into pellets by extrusion. The water used in this process allows a better control of the reaction temperature and of the viscosity of the solution. Polymer prepared in this way fits well for injection moulding, but is not very convenient for crystal type because of dispersants which may contaminate polystyrene. The suspension process with the batch-mix process are practically the most important.

Emulsion polymerization. Styrene, water, emulsifying agents (soap) and a water-soluble catalyst are poured into an autoclave. Reaction polymerization occurs between a temperature of 70°C and 100°C and, as before, it is well controlled due to the presence of water. Large quantities of soap used are difficult to remove from the polymer which is employed mainly to produce latex for coating or for making modified polystyrene by compounding with rubber.

*Polymerization with solvent.* This is a continuous process; the solvent is toluene or xylene and its major purpose is to remove the heat of the polymerization reaction.

TABLE	11.	10,000	TON	VYEA	R 81	YRENE	PRODUCTION
	Ma	nufactu	ring (	cosi	and	selling	price

	Unit	Unit cost	Annual quantity	Annual cost (10° \$/year)
Variable charges				
Raw materials				
Ethylene	Tons	110	3,360	370
Benzene	Tons	70	9,240	645
Utilities				
Electricity	10° kWh	10	1.300	13
Steam	Tons	1.6	100,000	100
Cooling water	10° mª	6	5,000	30
Process water	m <sup>a</sup>	0.2	35,000	7
Fuel	10 <sub>e</sub> koai	1.5	27,000	40
Labour				
Salaries and wages	Men-shift	5,000	24	120
salaries and wages.				30 50
TOTAL VARIABLE CHARGES				1,465
Pixed charges				
Depreciation at 12.5 per cent of tot	al investment			
Interest at 3.5 per cent of total inve	stanent			
Maintenance at 4 per cent of total :	investment			
General plant overhead at 2 per ce	nt of total inves			
			• • • • • • •	
Taxes and insurance at 1 per cent of	of total investme		•••••••••	
Taxes and insurance at 1 per cent of	f total investme	<b>mt</b>	••••	
Taxes and insurance at 1 per cent (	f total investme	<b>mt</b>		305
Taxes and insurance at 1 per cent (	f total investme	пат		
Taxes and insurance at 1 per cent of	f total investme	на Тота: Мани	U FICED CHARGES	
Taxes and insurance at 1 per cent of tota	of total investme	іні Тотаі Мани	L FIGID CHARGE	1,976
Not each flow at 20 per cent of tote Depresention provides	of total investme al investment .	іні:	VACTURING CORT	1,970 440 275
Not such flow at 20 per cent of tota Not income after taxes	of total investme al investment .	ни	VACTURING CORT	1,970 440 275 165
Not such flow at 20 per cent of tota Depreciation provides Not income after taxes Not income after taxes at 50 per c	of total investme al investment .	ни	VACTURING COST	1,976 440 275 165 330
Not each flow at 20 per cent of tota Not income after taxes	of total investme al investment .	ни	VACTURING CORT	1,970 440 275 165
Taxes and insurance at 1 per cent of Not each flow at 20 per cent of tota Depreciation provides	of total investme al investment .	INT	VACTURING COST	1,976 440 275 165 330
Taxes and insurance at 1 per cent of Not each flow at 20 per cent of tota Depreciation provides	I investment .	Int		1, <b>976</b> 440 275 165 330 1, <b>970</b>

	Uati	Unit cost 3	Annual quantity	Annual cos (10ª \$/year
Variable charges				
Raw material styrene	Tons	230	7,800	1.800
Utilities			,,	1,000
Electricity	10 <sup>e</sup> kWh	10	2.625	26.5
Steam	Tons	1.6	2.250	3.5
Cooling water	10 <sup>e</sup> m <sup>a</sup>	6	450	3.5
Process water	m <sup>a</sup>	0.2	30.000	6
<b>Fuel.</b>	10 <sup>e</sup> kcal	1.5	940	1.5
Catalyst and chemicals			<i>,</i> 10	7.5
Labour				
Salaries and wages	Men/year	5,000	8	40
salaries and wages				10
TOTAL VARIABLE CHARGES				1,896.0
Exad charges (see table 11 for distrib	ution)	•••••	· · • • • • • •	356.0
		MANU	FACTURING CORT	2,254
Not cash flow at 20 per cent of tota	l investment			210
Depresiation provides			• • • • • • •	310 195
Not income after taxes at 50 per ce	nt	•••••	,	115
Manufacturing cost		•••••	• • • • • • • • •	2,254
		• • • • • • •	•••••	4,4J4
Styrene sales				2.369
Styrene selling price (\$/ton) .				315

# TABLE 12. 7,500 TONS/YEAR POLYSTYRENE GENERAL PURPOSE PRODUCTION Manufacturing cost and selling price

A mixture of styrene and solvent is introduced at the Utilities requirements top of the first reactor and fed from the bottom into a second and afterwards into a third polymerization reactor. The reaction is started by heating and as it proceeds from one reactor to the other, the viscosity of the solution increases. From the bottom of the third reactor, the solution is passed into a devolatilizer vessel, kept at low pressure, where solvent and univacted monomer are removed and recycled. The molten polymer is pelletized by extrusion.

Polymerization with solvent involves lower rates of reaction and lower molecular weight of products in comparison with those obtained in bulk, suspension or emulsion. Moreover, it is difficult to remove the solvent completely; polymer being already in solution is used for lacquers.

### Economics of polystyrene manufacture

The elements of operating cost for a 7,500 tons/year polystyrene general purpose plant are given below:

### Investment

Process units (\$ million)	•	•	•	•	•	•	•	•	1.55
Raw material accountion (tons/yvar)									7,800

Electricity (10 <sup>e</sup> kWh/year) .							,			2,625
Steam (tons/year)					•					2,250
Couling water (10 <sup>#</sup> m <sup>3</sup> /year)										450
Process water (m <sup>s</sup> /year)				•	•					30,000
Fuel (10 <sup>e</sup> kcal/year)					•	•				940
Catalyst and chemicals consum										7,500
Labour (men/shift)		•	•		•		•	•	•	2

Manufacturing cost and derived selling price for such a unit are presented in table 12.

### Conversions of plastics into ond-products

Everybody knows the two extreme rings of the chain linking crude oil to products made with plastics which everyday gain new outlets in domestic or industrial fields. We have already talked about the transformation of oil into plastic materials, which can be considered as the beginning of a new way towards the manufacture of end-products.

This chapter deals with the last stage of transformation to be carried out before reaching consumer or industrial goods, and their applications in the case of polyethylene and PVC.

Several techniques have been developed for converting plastics into end-products. They are all convenient for treating PVC, polyethylene or polystyrene, but some of them are more or less used according to the plastic type; for example most of the polysty.ene is converted by injection moulding.

The main conversion processes are listed below with a brief description of their method of operation.

Extrusion is the process of applying heat and pressure to melt plastic and force it through an accurately dimensioned die to produce continuously shapes in the form of: unsupported films; sheeting; tubes and other profiles; film for coating paper and paper board, metal foil, cellophane and other substrates; coating around wire or cable.

Injection moulding is after extrusion the most widespread conversion process. Plastic is heated and melted to a viscous liquid into a heating cylinder; then by means of a ram it is forced into a relatively cool mould shaped in the form of the desired object.

Blow moulding has a specific production in containers of all sizes from tiny flasks to carboys. A pipe-shaped preform is either extruded or produced by injection moulding and when still soft it is blown by means of compressed air to conform to the shape of the bottle mould.

In calendering, softened plastic passes through a series of heated stell-rolls; the first pair of rolls flattens the paste into a sheet, the thickness of which is gradually reduced until we get a film of the desired thickness. Calendered films have better tensile properties, a more accurate and more constant thickness than extruded films. Coating is a process for laying plastic, in slight thickness generally, on a substrate such as fabric, paper, or metal. This layer has to fulfil several functions:

Protection of substrate against corrosion, impacts, wear. Improvement of the surface roughness of the substrate. Decorative purpose.

For the lining of paper or fabric a continuous film is deposited by spread-coating or by calendering. In the case of spread-coating plastic is used in the form of a polymer solution, latices or dispersion; for example, PVC is dispersed in plasticizers to make plastisols.

Dip coating is another coating process mainly employed for covering versatile shapes of pieces (in metal generally) with plastic. Large pieces may not easily be treated in this manner; therefore plastic in solution is sprayed with a special spray-gun.

Eventually, a new coating technique is to fluidize plastic powder and to dip the hot piece into this fluidized piece.

### POLYETHYLENE

Table 13 gives techniques for converting polyethylene and main end-uses; table 14 shows the relative importance of its applications in the United Kingdom and the United States; there is no statistical basis for other countries; however, these two markets are a good pattern for comparative purposes and extrapolation.

### Polyethylene compounding

Because of the molecular structure of polyethylene, this plastic has a good flexibility over a wide-range temperature and it is not compatible with plasticizers. Therefore, polyethylene does not claim plasticizers for compounding as PVC does.

	→ Extrusion	Pipes, garden hoses Bags Blown film and flat film, sheets Wire and cable coating Extrusion coating of paper, paper board, cellophane, metal foil, cloth, glass fibre., etc. Filmments
Pol! THYLENE Compounding →		Household erticles Cape for bottles Industrial items
	Mow moulding	Bottles and containers Toys
	Calendering	Electrical tage
		Containers Large and flat contour shapes
	Spray-coating or dip-coating	Metal protestion
		r Hollow objects

TABLE 13

		United 1	Ci <b>ned</b> om			United	States	
tons)	1961		1962	· · · · · · · · · · · · · · · · · · ·	1961	· · · · · ·	1962	•
Whole consumption (metric								
tons)	78,000		103,000		555,500		625,950	
Low-density								
			90,000		449,400		478,750	
		26.5		25.2		15.5		14.3
		12.5		9.5		4.3		3
		33.7		37		49.2		49.5
Wire and cable coating	1	14.3		16		12.9		13.
Extrusion coating		4.5		4		9.3		14.9
Pipes and profiles		6.5		5.3		5.6		2.
Miscellareous		2		3		3.2		2.3
ligh-density								
Consumption (metric tons) .	7,200		13,000		106,100		147,200	
		55		44		35.5		17.6
Blow moulding.	1	4		34		46.2		50.6
Film and sheet				2		3.7		4.8
Wire and cable coating				5		1.2		2
Fipes and profiles		3		3		8.5		9
Extrusion coating						1.2		1
All other extrusions.				11				
Miscellaneous	1	1		1		3.7		15

# TABLE 14. POLYETHYLENE BREAKDOWN INTO END-USEN (IN PER CENT OF CONSUMPTION)

Nevertheless, additives are used to improve certain properties of the basic polyethylene.

- Antioxidants (aromatic amines) must inhibit oxidation, occurring mainly at elevated temperatures, under all conditions of storage, processing and service of the end-products.
- Carbon black must prevent degradation of polymer from ultra-violet rays and thus extends external uses of polyethylene.

### Pigments.

Fillers are seldom added, sometimes the resin is blended with polyisobutylene or butyl rubber to make it more flexible at low temperatures and to increase its resistance to stress-cracking.

As for every polymer, the objective to obtain by compounding polyethylene with miscellaneous ingredients is a homogeneous mixture that is determinant for mechanical properties and aspect of end-products.

According to the grade of homogeneity to be reached, two routes are possible for compounding:

First, polyethylene is removed directly from the reactors into a specially designed extruder with an under water pellet cutting head which supplies it in the form of cylindrical or cubic pellets ready to be used by plastics converters.

Internal mixers are used before the extrusion stage in order to improve homogeneity; this second way is the more often followed to obtain pellets. Most producers deliver pelletized polyethylene, but growing requirements and attractive outlets for powdered polyethylene, the applications of which were discovered about four years ago, urge some producers to grind polyethylene into powder.

### **Polyethylene** applications

Before examining the principal applications one should consider the polyethylene properties which determine its uses. Density is the major characteristic of polyethylene; it ranges from 0.910 to 0.940 for low-density type and from 0.940 to 0.965 for high-density; only polypropylene with a 0.885/0.9 density can surpass polyethylene in lightness. As said before, high-density polyethylene is rigid and low-density flexible; the following properties are improved as density increases : yield strength, chemical resistance, impermeability to liquids and gases (poor for low-deucity), heat resistance. All formulations have good resistance to moisture, to corrosion of most chemicals at the usual temperature; beyond 60°C polyethylene performances are lowered and it may be softened or dissolved by some acids (nitric acid), organic solvents; polyethylene is cracked by concentrated detergents.

Polyethylene has excellent dielectrical properties, highly desirable in electrical insulation, mainly in the high-voltage and high-frequency field.

This brief survey of polyethylene characteristics would be incomplete without mentioning its weakness to resist against flames and sunlight; nevertheless these two drawbacks are eliminated by addition of carbon black.

### Film and sheet

So far, every year more polyethylene resin has been consumed for film making than for any other end-use. In the United Kingdom and the United States at least one-third of all polyethylene produced is converted into unsupported film and over 75 per cent of these films is used for the packaging of foods, fresh vegetables, textiles, soft goods, toys, chemicals, etc. When impermeability properties are of secondary importance, polyethylene gains advantage over rival plastic films — specially PVC film due to its more attractive appearance and gloss.

One recent outlet which could spur ahead the polyethylene market would be the development of plastic bags for fertilizers, cements, and any powdered materials.

The main attractions of these bags are:

Their weather-proof qualities which enable the contents to be stored in the open oven at low temperature.

- The savings in space, handling and transport, which can be flected because of their lightness and flatness when stored.
- The competitive price as compared to the price of waterproof paper bags.

In the bags field, competition will be severe with PVC bags which have better properties as to impermeability, sealing and prin ing, but are less resistant to temperature.

Other non-packaging applications exist for polyethylene in agricultural and construction uses: mulching and row covers, silos, liners to prevent scepage in farm reservoirs.

Finally, polyethylene sheet may be thermoformed into miscellaneous boxes for packaging or other large items with complex contours (refrigerator door panels, picnic plates, etc.).

### Wire and cable coating

Owing to high electrical resistivity and dielectric characteristics, polyethylene is used for electrical insulation or as an outer jacket on power cables, telephone lines, television lead-in wire and appliance wire, where it serves both as insulation and a barrier against moisture, weathering and abrasion. To improve its environmental crack resistance polyethylene is usually compounded with polyisobutylene or synthetic rubber.

An alternative extrusion process allows coating with foamed polyethylene by adding a blowing agent to plastic; cells filled with air withheld in polyethylene impart better dielectrical properties and lightness to the insulating layer.

### Bottles

Polyethylene is blow-moulded into numerously shaped bottles for drugs, foodstuffs, chemicals and cosmetics. High-density polyethylene is expanding rapidly in this field because of its lower permeability, preventing diffusion of volatile substances and providing better cracking resistance to chemicals, mainly liquid detergents or powdered kitchen cleaners.

### Pipes

The principal advantage of the polyethylene pipe is its flexibility which allows lengths up to 450 m with a diameter of 5 cm and below to be coiled for shipment. This results in great ease of installation; machines are able to bury almost continuously pipes in case of water adduction, for example. Polyethylene pipe finds steadily increasing acceptance for farm, mine and home uses, primarily in the transportation of cold water or milk, fruit juices, etc., in food processing plants

### Extrusion coating

Polyethylene is coated on paper, paper board, cellophane, polyester film, aluminium foil, glass fibre, and cloth. The main purpose of coating a substrate with polyethylene is to combine the properties of the two materials. Polyethylene-coated materials have low moisture vapour permeability, good flexibility, high chemical inertness, good heat sealability, absence of taste, odour and toxicity.

These new materials find various uses in bags for packaging foods (milk), chemicals, etc.

### Houseware articles

High-density polyethylene is very suitable for making items that must be rigid, not heavy, resistant to heat, to chemicals and to fracture, and which are used for kitchenware (buckets, spoons, wash basins, strainers) and in washrooms (wash bowls) as well as in gardens.

### Industrial articles

Few industrial purpose objects are made with polyethylene. We can mention fan blades, tanks, but metal surfaces of devices working under severe corrosion can be coated with a layer of polyethylene by spray-coating or dip-coating; fittings and pipes are so protected against corrosion and scales.

### Miscellaneous

Low-molecular-weight polyethylene serves to prepare emulsifiable or non-emulsifiable waxes. The highest outlet for the first ones is floor polish, and moreover they are used to impart wash and wear properties to textiles. Non-emulsifiable waxes are used for coatings for paper and paper board, rubber. adhesives and printing inks.

Powdered polyethylene has found recent applications in metal coatings, automobile carpets, rotational moulding of toys, large tanks, etc.

Cellular polyethylene is used for making buoys, dock fenders, boat bumpers.

Ropes for fishing nets, industrial fabrics.

### POLYVINYL CHLORIDE

Table 15 shows the conversion processes of PVC and its main applications. In order to judge the selective importance of these applications, refraces should be made to table 16 giving the distribution of PVC occurrent in the United States, France, Great Britain and Italy in 1962 as well as the evolution of this distribution. The figures cited should be looked upon with caution owing to a lack of coherence in the definition of identical terms used in different countries.

### **PVC** compounding

The PVC obtained at the outlet of the polymerization reactors cannot be used as such for the manufacture of end-products. Compounds are propared — on the basis of PVC — while incorporating various materials which selectively modify the physical or chemical properties of pure PVC, depending on the utilization of the articles made.

These additives are divided into several generic groups according to their essential functions

### **Plasticizers**

These are special solvents of very low to zero volatility. which change the flexibility or the plasticity of PVC. The pure PVC is indeed a very hard material which has to be plasticized, on the one hand to facilitate the ourversion processes, and on the other to improve the shock resistance of the end-products. According to the content of plasticizers one distinguishes between rigid PVC (amount of plasticizer below 5 per cent weight of the mixture) and flexible PVC (for which the plasticizer content can reach 50 per cent). The Dioctyl Phthalate (DOP) is one of the principal plasticizers combined with PVC, but the choice is at present exerted amongst a great variety of products. The importance of the consumption of plasticizers is another feature of the evolution of these chemical products, for which a special branch of organic chemienty is in development in 1962 the United States produced 354,000 tons of plasticizers for the plastics industry as a whole, 106,000 tons of which heing DOP

### Stabilizers

Under the influence of light (1, V) or of heat, the macromolecule representing the PVC is decomposed and discharges hydrochloric acid, this macromolecule modified in this way catches oxygen. These internal modifications which degrade the macromolecule, reduce the mechanical properties, change the colour and the appearance of the end-products. The stabilizers, in general compounds based on tin or zinc, retard or reduce these phenomena which involve ageing (influence of light, of atmospheric agents) or conversion (influence of heat) of PVC.

### Fillers

The properties of PVC can further be modified by mineral compounds (asbestos, seapstons, slate powder, kaolin) or by other polymors like butadione, aerolonstrils, polyvinyl sostate. The objects of research are numerous improvement of the mechanical properties, in particular

	nen ander ander ander ander ander ander ander ander ander ander ander ander ander ander ander ander and and and	· • •	Controlation processes	e en en en en en en en en en en en en en
	Later, esgansath, e		Paintings	
			Blowing agents	Pearse
	PLANNING	+	Retational mouthing	Yaya
			Coating	Spread coating or valunduring of doth or paper
				Conting by dipping, spraying of anntallis parts
			<b>Betragten</b>	Right rakes, Realists prices Graning electrical releas Right PMC electric, corregated -leasts, lange Take or classis for Browing
	PVC :::::::::::::::::::::::::::::::::::	1	Planatering	Parlinging (sigid chaote)
<b>PVC</b>	(compound or PVC punder)	•	býmiun seeding	Bartolo garto (plantichani PVC) Trito Billingo (sigit PVC) Tupi, dinas
			Information Meridag	Butthe, container
			Calo-schuring	No er dans for fantag Pudla PVC dans Nas
				Film

TABLE 15

-

### TABLE 16. DISVERSION OF PVC CONSUMPTION

( In per cent of world consumption)

	v	ution State	~		Pressee		(je	est Brint			Inaly	
		1961	1962	7 <b>9489</b>	1961	1962	/960	1961	/963	/1400	1961	2962
Fotal consumption (19º tono).	407	437	185		160	136		120	135			115
Nyd PVC												
Tubes and piper Profiles			1.6 2.2	,		15	9.5	8	4.5 3.5			<b>22</b> 17.1
Nomble PVC												
Cable and whe ceating	(Basta	dad in Ming an	15.3 4	18		17	17.5	15	19			13
Floaring	entru 17.6	<b>ntan)</b> 19.1	21	16		Ð	6.5	9	12			
Films and shorts total (a) Unsuggested	28.6	24.6	12	24		28 10.5	24	25 5	<b>20</b> 7			18
(b) Supported	(Brah studi	ndend in h annd		12		10.3	12	,	,			•
Chath and more contine	7.1	r contin 7 5	-									
Moulding and entrusion	33.4		•	8								5
(d) Extrusion			31	9		6.5	10.5	12				
Maadimaan	16.3	16.0	38.4	6		2	20	26	26			15

of wear resistance, chemical and electrical resistance, of the heat or odd resistance. Moreover, the type of fillers plays an important role in the stabilization of the PVC compounds, the surbon black which absorbs the UV, protects the PVC against the influence of light. A different support is the reduction of the cost of the compounds by incorporation of these fillers (particularly of seapstone).

### Pigmonte

Generally, PVC is coloured by organic or minoral pigments, these are finally dispersed pewders minod intimately with PVC

# Various additives

For special applications PVC to mined with fungicides, antistative, blowing agents, which by heating or chemical reaction disongage gases in the inner material, thus converting it into cellular elements.

It is important for the quality of the and-products quarticularly films) to proper very bettergeneous comprends, they can be obtained by compressing exercises excited out in machines that researcd one another in an almost constant order.

- A preminer, a double-walled vessel and a propeller or blade mixer, into which the ground pigments, stabilizers and plasticizers are introduced.
- An internal miner (Banbury type) operating batch-
- A cylindrusal open minor which delivers the minture in the form of a plastic mass sufficiently homogeneous and suitable in this form to be converted — e.g. into flooring — by calendoring. But in this form the minture is mather to be easily removed nor to be used in any process necessitating an extrusion or an injection. Thus, the final stage to accomplish is the granulation which converts the PVC compound, by passing through an entruder, into pollets.

In order to be preditable, the preceding operations have to be carried out on large quantities of PVC; only manufacturers or very large constances of PVC are in a position to encoute them under these conditions.

Anyway, PVC has been propered by suspension polymerication, which has a high case of abcorption of phosticians, owing to which dry blonds can be obtained in one single miner; the minture is withdrown in the form of a very fluid periodic which does not applements. This periodic can also be used in specially constructed, double-ensure extruders.

### **PVC** applications

It is not possible to door up a complete list of all PVC applications, the markets of which are developing every day. We will make a classification by half-finished products and we will examine in more detail in each of these groups the most important uses.

### Rigid PVC

The most outstanding qualities of rigid PVC are: chemical inertness, resistance against atmospheric agents, chemical resistance, electrical resistivity, lightness, stability, fireproofness. These qualities determine for the greater part the use in the open air of articles made with rigid PVC. A shortcoming is that PVC has a bad resistance against cold.

Pipes, tubes and fittings. Used in building works, in agriculture, in chemical engineering, for the drinking water supply and distribution, for the transport of waste water or even of very corrosive liquids (salted solutions). At the present moment the use of pipes is limited to fluids of which the temperature does not permanently rise above 60°C. In order to completely satisfy the requirements raised by the distribution of hot and cold water in buildings, rigid PVC would have to be resistant to a continuous temperature of 100°C; some manufacturers state having obtained a PVC with this property. Moreover, rigid PVC tubes are used as insulating pipes of electric wire.

The following figures show the share taken by pipes in the rigid PVC market:

	Tone of a	igid PVC use of pipes	and mbrz	
	1960	1962	1963	1968
Federal Republic of Germany		20,000		
United States		8,150	10,400	52,000
Prance and a second second	6,150	12,000		
United Kingdom		6,000	6,540	
Raly		25,000		

The use of PVC pipes was first developed in the European countries — particularly in Italy — which have now resolved most of the technical problems of laying and adjusting, which restrain the use of these pipes. This explains partly the small importance of rigid PVC pipes in the United States and the increase foreseen until 1968.

Profiles. Mainly used in building works as gutters, window frames, parts of shutters or blinds, corrugated shoets for roofing. In 1962 in the United States 11,300 tons of profiles were produced and 11,000 tons of corrugated shoet. The forecasts for 1968 are as high as 43,000 tons of profiles and 45,000 tons of corrugated sheet.

Other user. Rigid PVC has found new markets in the manufacture of containers for edible oil, detergents, lubricating eils, fruit juices, winne, yoghowri and for complex PVC films — paper or PVC films — shuminium feil for packaging of edible fats. The United States estimate to have a consumption of 22,660 tons of rigid PVC for these uses in 1968.

- Fibres for the manufacture of industrial fabrics (special filters), of curtains, etc.
- Manufacture of materials used in the chemical industry for the storage or the transport (pumps, ventilators) of acids or corrosive liquids.
- Packaging of foodstuffs prepared by thermoforming from rigid PVC sheets.

### Flexible PVC

Cable and wire coating. These conduits are coated with two layers, the first ensuring electrical isolation, the second being a protecting layer consisting frequently of a mixture of PVC-rubber-butadiene-acrylonitrile. In case of conduits through which pass high-frequency currents (radar, telecommunication) the first layer is made of polyethylene which has better dielectric properties.

Films and sheets. The distinction between films, sheets and plates is based on the difference in thickness of these half-finished products: the thickness of films is less than 0.5 mm, that of plates greater than 2 mm and that of sheets lies between 0.5 and 2 mm. The main features of PVC films are impermeability to water and gas, mechanical resistance (wear and tear) and inflammability.

These films are used:

- In a riculture, to coat water reservoirs or irrigation canals and to suppress losses by seepage, for the rapid construction of greenhouses and silos. In this field competition is vital with the polyethylene films;
- In the clothing industry to line fabrics or to serve as such for the manufacture of ready-made clothes;
- In the automobile and aeronautical industry, in the furniture industry to cover seats, to manufacture curtains and table cloths.
- In the packaging of non-edible products.

A recent and promising market is the manufacture of bags (0.25 mm thickness) for cement concrete, fertilizers or any other powdery product requiring a protection against humidity; compared with the traditional bags, of paper or cloth, they are light-weight, not bulky when empty and impermeable, thus easily stored in the open air.

Flooring. They are presented in the form of tiles or strips. The tiles are prepared starting from a fairly charged mixture, mostly asbestos (which may reach 70 per cent weight of asbestos). These floorings are very easily laid, they offer a great variety of colours, an excellent wear resistance and are easily maintained.

PVC is also used in the manufacture of linoleum, together with linseed oil, wood and cork powder.

Foams. The different applications of foams result from their properties: lightness, acoustic and thermic isolation, imputrescibility, inflammability, chemical shock resistance.

They are used in the cold industry and in building as insulating material, in packaging as a protection against shocks, in the automobile industry as a trimming against noise; novel foams, with open cells, contrary to entirely closed cells, ensuring the expansion of the proceeding foams, are finding applications in domestic arts: carpets, mattreess, seat coverings, etc.

Coating. The coating of cloths or paper consists in spreading out a paste of low viscosity obtained by cold mixing of plasticizer and PVC (plastisol) with the aid of a coating frame or a calender. The coated cloths find applications as Morocco-leather tannery, travelling articles, furniture, clothing, shoes, industrial fabrics, furniture covering; coated papers are used for wall decoration, in the books industry, etc.

Coating by heat or cold dipping permits the laying of plastisol on articles (in general metallic) of the most varying forms. For very bulky matter, of which the surface to be coated is large, it is preferred to spray the plastisol with the aid of an electrostatic pistol, eliminating practically every loss by projection.

Finally, a new method of coating metallic parts consists of fluidizing a mixture of PVC powder and to dip the preheated metal into it at a temperature which is higher than the melting point of the mixture.

Other uses. Numerous pieces made by injection moulding, which are used in the electrical industry (connections, handholds of electrodes, insulating pushbuttons), parts for vacuum cleaners, etc.

Toys, shoe heels — by rotational moulding.

Garden hoses.

Records for phonographs.

Driving belts.

# ECONOMICS OF PVC CONVERSION IN INDUSTRIAL AND CONSUMER GOODS

### Pipes

### Annual production (6,000 hours/year)

Size of pipes	Operating pressure (kg/cm²) at 20°C	Total iongth go hm
40 × 30	16	312
50 × 46.4	4	<b>w36</b>
63 × 53	10	94
63 × 57	6	136
110 × 102.8	4	144
110 × 92.4	10	122
125 × 117	4	56.5
160 × 150	4	36
140 × 144	6	43
257 × 234	4	<b>57</b> .5

Raw materials (tons/year)	
Utilities:	
Electricity (kWh/year)	
Water (m <sup>#</sup> /year)	
Investment (\$)	415,000
Operating manpower	
Labourers (3 shifts) 54	
Foremen (3 shifts)	
Engineer	

Notes

(a) Pipes are made with PVC powder compounded with stabilizers and dyes.

(b) investment costs include the following devices, without erection (basic price for Europe 1963). PVC storage (supplying production during one month). Powder delivery.

Double-screw extruders. Water bath for cooling, pipes take-off.

Cutting machine.

Socket forming oquipment.

(c) Investment costs for the same production of steel pipes or plastic pipes are supposed to range from 5 to 1. Moreover, plant erection and starting-up take more time in case of manufacturing steel pipes.

### Bags

Annual production (6,000 hours/year)

\$.000.000 bags

Raw materials		
PVC (tons/year)	1,300	
year).	1,100	
Utilities		
Electricity (kWh/year)	1,03 <b>8,000</b>	
Investment costs (S)		250,000
Operating manpower		
Labourers (3 shifts)	51	
Foremen (3 shifts)	12	
Engineer	1	

Netes

cities of PVC bags are 25 kg (wall thickness 0.2 mm) (e) TÌ d 50 kg (thicks an 0.3 mm).

de the following materials without erection : ge (supplying production during one month). in in (A) lev PVC and ad ï, άy.

# 2. LOW-DENSITY POLYETHYLENE — THE WORLD MARKET

K. E. Cosslett, U.S. Industrial Chemicals Co., USA

Almost 30 years have passed since two English scientists produced an unknown white, wax-like substance while experimenting with the effects of high pressures on chemical reactions. The puzzling result was attributed to a leak in one of the joints of the reactor.

Not very many years later, this "accident" — called polyethylene — helped win the Battle of Britain as the insulation for flexible, high-frequency radar cable.

Since it was released for non-military use after the Second Werld War, polyethylene has recorded one of industry's most astonishing growth records. It is almost impossible in many parts of the world to visualize modern society without this remarkably versatile plastic. So many industries — food, drug, packaging, transportation, communications, agriculture — now market products that are more economical and more convenient to use because of polyethylene.

Take packaging for example. At the time of that reactor malfunction 30 years ago, such items as unbreakable bottles, liquid-ho'ding paper cartons, no-dent cans and moistureproof shipping bags were not even in the idea stage. Now, these packages are commonplace in many countries. Polyethylene — in the form of a transparent film, a coating, or a moulded or extruded shape -- has made it all possible. In 1963, the countries with free enterprise economies used 1,535,000 metric tons of lowdensity polyethylene resin. This discussion will be limited to low-density polyethylene — that is, polyethylene made from high-pressure polymerization, since this type of polyethylene offers the greatest immediate potential for countries that may be contemplating the start of polyethylene operations.

Over the past six to eight years, a dramatic change has been taking place in world production and consumption of low-density polyethylene resin.

In 1956, the United States accounted for about 75 per cent of the 345,000 metric tons produced in the world (see figure 1). Now, even though United States production is 3 times what it was in 1956, other parts of the world are catching up. Europe's production alone now rates at about 60 per cent of United States production, and its annual rate of growth over the past three years has been 32 per cent compared to 13 per cent for the United States.

In 1963, European production was almost in balance with European consumption. Next year, European production will pass consumption for the first time, and by 1966 exceed it by almost 20 per cent.

It is likely that by 1970, the United States share of free world low-density polyethylene consumption, at slightly more than 1,360,000 metric tons, will represent less than 40 per cent of the 3,720,000 metric ton projected total.

Per capita figures present an equally dramatic picture. In 1960, per capita consumption of low-density po vethy-

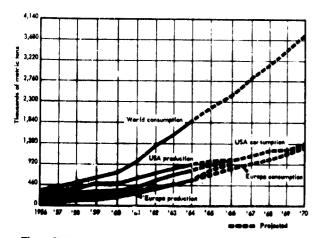


Figure I. Production-communities of low-density polyethylene, United States and Barage

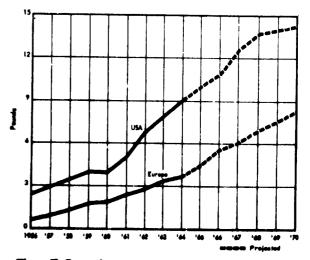




TABLE 1. MAJOR MARKETS FOR LOW-DENSITY POLYETHYLENE

- 1. United States
- 2. Japan
- 3. United Kingdom
- 4. Federal Republic of Germany
- 5. Italy
- 6. Canada
- 7. France

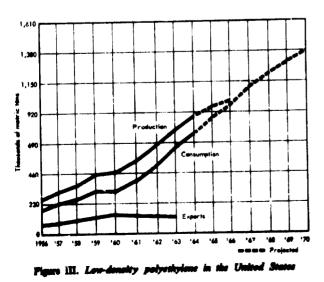
lene in Europe was some 1.7 pounds compared to almost 4 pounds in the United States. In 1963, Europe's per capita consumption reached 3.2 lb., the United States 7.2 lb. By 1970, it is estimated that European per capita consumption will be higher than that of the United States today. Conservative projections put European consumption at 8.4 pounds per head in 1970, the United States at 14.5 pounds per head. Thus, in 10 years, Europe's per capita consumption will have increased fivefold while that of the United States will have tripled.

The seven major markets for low-density polyethylene are: the United States, Japan, the United Kingdom, the Federal Republic of Germany, Italy, Canada and France.

In the United States, polyethylene's past, present and future looks like this:

Production has jumped from about 260,000 metric tons in 1956 to just over 450,000 metric tons in 1960 and to almost 800,000 metric tons in 1963. The upward spiral will continue, but the rate of increase will decline. A figure of 1,000,000 metric tons is predicted for 1966.

During the growth years of the late 50s, United States production consistently exceeded consumption in the United States by about 30 per cent due primarily to the demand from the non-producing world areas. In recent years the gap in percentage has been narrowing although, of course, the poundage gap is still large — over 135,000 metric tons. Over the next few years the production-



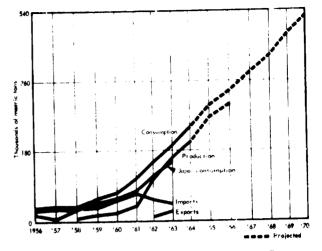


Figure IV. Low-density polyethylene in the Far East

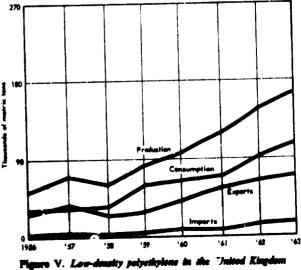
consumption balance will improve consideratiy as non-United States production capabilities increase.

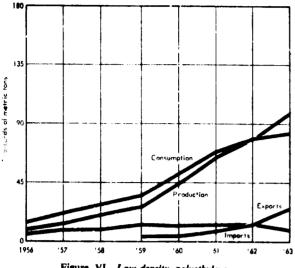
Although no other single nation uses nearly the volume of low-density polycthylene that the United States does, some other countries have equally fantastic growth stories to report. There is no better example than Japan.

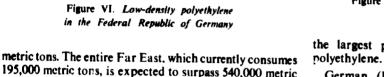
At 175,000 metric tons per year, Japan is now the second largest producer of low-density polyethylene. In 1956, this country had no local production whatsoever. It imported all the 18,500 metric tons of low-density polyethylene that it used.

Its first recorded local production was in 1958. By 1960, it was producing over 30,000 metric tons a year, fourth highest in the world. Consumption, which still included sizable imports, was third highest at 55,000 metric tons in that year.

Today Japan exports 20,000 metric tcns of lowdensity polyethylene per year and consumes 155,000







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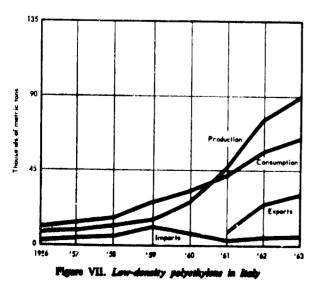
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195,000 metric tons, is expected to surpass 540,000 metric tons by 1970, and production should almost double within the next three years.

Of the European nations, the United Kingdom — with production of more than 160,000 metric tons in 1963 — is the leader. Almost-one half of this is exported, but domestic consumption still runs at almost 110,000 metric tons per year, due to imports.

As shown in figure V, this represents a 200 per cent increase in production since 1956, and close to a 300 per cent increase in consumption.

In the Federal Republic of Germany, like Japan, growth of polyethylene has been dramatic. Production has risen from 9,000 metric tons in 1956 to 45,000 metric tons in 1960, and to 100,000 metric tons in 1963. That is more than a 1,000 per cent increase in seven years. The Federal Republic of Germany is (after the United States)



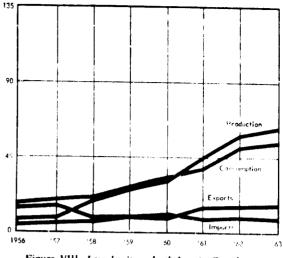


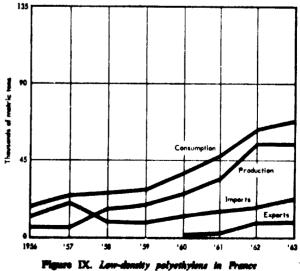
Figure VIII. Low-density polyethylene in Canada

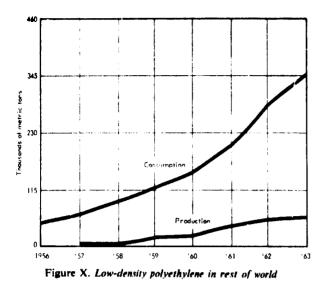
the largest producer of high-density or low-pressure polyethylene. The process originated there.

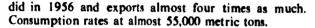
German (Federal Republic) consumption of lowdensity polyethylene runs at about 85,000 metric tons per year today, and exports amount to 25,000 metric tons. Imports, which reached a high of 14,000 metric tons in 1962, are definitely on the decline.

Number five is Italy. Local production is 135,000 metric tons at present compared to 8,000 metric tons in 1956 and slightly less than 27,000 metric tons in 1960. Italy, like the United Kingdom and the Federal Republic of Germany, is a major exporter with one-third of its production going outside the country. As recently as 1960, Italy exported no low-density polyethylene.

Canada in 1956 produced 8,000 metric tons, exported 4,500 metric tons and imported 14,500 metric tons. Today, Canada ranks sixth in world production at almost 64,000 metric tons. It imports about half as much as it







In France the story is similar to other European countries. France's total production was less than 5,500 tons in 1956. That is less than any single presentday United States plant. By 1960, France had increased its capacity for low-density polyethylene to 26,500 metric tons, and the country had started to export resin. Today's French exports are five times what they were in 1960, and almost double the nation's total home production in 1956.

Local production at present is almost 55,000 metric tons. The country imports about one-third of its consumption of 68,000 metric tons.

The rest of the world market for polyethylene also has demonstrated healthy growth. In 1956, total production for all free-world nations outside the present top seven was zero. Consumption, however, totalled 45,000 metric tons -- approximately 15 per cent of the world total. In 1960, the figures for all nations except the top seven were 25,000 metric tons produced and 150,000 metric tons consumed.

Currently, production outside the United States, Japan, United Kingdom, Federal Republic of Germany, Italy, Canada and France stands at more than 100,000 metric tons or about 6.5 per cent of the world total Consumption, however, is up to almost 345,000 metric tons or 22 per cent of the world total — proof that there is enormous interest in polyethylene among nations that today have little or no production capability.

Taken on a per capita basis, present market trends appear even stronger. Among the seven major markets, the United States is first today with 7.6 pounds per head followed by Canada at 6.4 pounds, United Kingdom at 4.5, Japan at 3.5, Federal Republic of Germany at 3.3, France at 3.1 and Italy at 2.9.

For comparative purposes it is interesting to note that in 1960, Canada had the highest *per capita* consumption among these nations with 4.10 pounds, followed by the

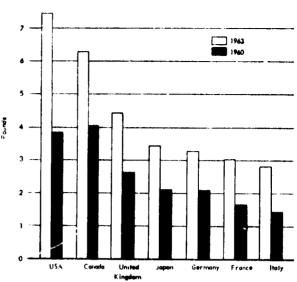


Figure XI. Low-density polyethylene per capita consumption

United States at 3.93, the United Kingdom at 2.7, Federal Republic of Germany at 2.16, France 1.80, Italy 1 52 and Japan 1.20.

What are the end uses that have carried low-density polyethylene to such phenomenal heights?

The biggest single use — in the United States, and in most other countries as well — is flexible film, about three-quarters of which goes into packaging applications. United States film and sheet makers now consume lowdensity polyethylene resin at a rate of 285,000 metric tons a year. That is 36 per cent of all United States polyethylene volume. Injection-moulding applications use 118,000 metric tons or 15 per cent, extrusion coating 93,000 metric tons or 15 per cent, extrusion coating 93,000 metric tons or 12 per cent and wire and cable insulation — the original application — 84,000 metric tons, or 11 per cent. Other major uses include pipe and blow moulding.

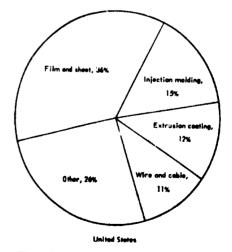


Figure XII. Low-density polyethylene end-use

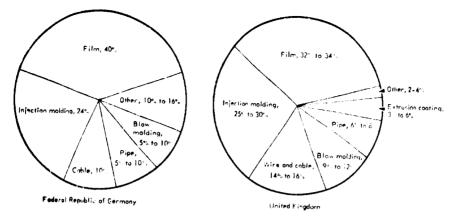


Figure XIII. Low-density polyethylene end-use

It is not always possible to obtain this type of data for other countries. However, film and injection moulding generally rate first and second respectively among major consuming nations. After that there is little correlation.

Estimates on the United Kingdom market give film 34 per cent, injection moulding 30 per cent, wire and cable 16 per cent, blow moulding 12 per cent, pipe 8 per cent and extrusion coating 6 per cent.

In the Federal Republic of Germany, film is credited with 40 per cent of the nation's usage, injection moulding 24 per cent, cable 10 per cent and pipe and blow moulding 5 to 10 per cent.

One would think that a material that has enjoyed such huge success in so many areas of the world would have just about run out of new applications. But nothing could be further from the truth.

In film, for example, polyethylene now serves more of the bread-wrap market in the United States than either of the traditional wrapping materials, cellophane and waxed paper. Polyethylene costs less and keeps bread softer longer. A similar trend exists in other countries where a lot of bread is wrapped.

Increased use of polyethylene film packages for consumer products parallels increased acceptance of the supermarket and its shelf life is vital when the product must

TABLE 2. NEW USES FOR LOW-DENSITY POLYETHYLENE

Flim for :	Powdered resin for :
Breed wrap	Carpet coating
All-plastic shipping bags Mulch	Rotational moulding
Green houses and silos	
Extrusion coatings for :	Wire and cable coating for :
Milk cartons	Submarine cable
From-food cartons	Telephous exchange cable
	Minule cable

sell itself. And packagers and retailers throughout the world have found that polyethylene film serves well on both counts.

Industrial packaging may be an even more important area of polyethylene usage in many areas of the world. In the United States about 50 million heavy gauge polyethylene bags are being used this year for fertilizer packaging alone, and the usage is growing very rapidly. Other industries, especially the chemical industry and segments of the mineral products industries and food industry, are beginning to convert from paper to allpolyethylene shipping bags.

The trend to plastic shipping bags is even stronger in the United Kingdom, and interest is high in many other countries, particularly where products such as fertilizer have previously been shipped in bulk.

Polyethylene's basic advantage here is its resistance to moisture. An all-polyethylene bag is essentially a waterproof container that can be stored indoors or outside without permitting water to contaminate the product. It also has a higher burst strength than paper. In the United States the plastic bag and the multi-wall paper bag are very close in cost. In many areas of the world, however, paper costs are extremely high and the polyethylene bag can prove significantly cheaper.

One of the newest polyethylene products is powdered polyethylene — in other words, the resin is sold in powdered form instead of the conventional pellets.

Apart from packaging, polyethylene film (frequently black-pigmented) is gaining steadily as an agricultural material. New automated methods for laying the film should make this superior mulch available to many more farmers throughout the world.

Extrusion coating of paper and foil has been booming in the United States since the start of the sixties. Only about 27,000 metric tons of low-density polyethylene were used for extrusion coating in 1958 in the United States compared to over 90,000 metric tons now. The main reason for this has been the switch from wax coatings to a smooth leakproof polyethylene coating for consumer milk cartons.

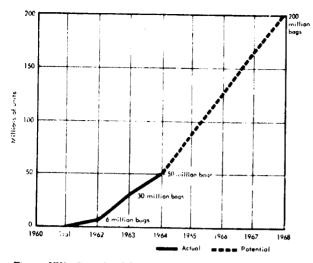


Figure XIV. Growth of heavy-duty polyethylene shipping bags in the United States

In other countries, extrusion coating has been slow to gain a foothold because of the sophisticated technology and machinery involved, and the relatively small use of milk cartons. There is, however, a growing acceptance for such foods as soft cheese and salads in cartons coated with polyethylene.

Frozen-food cartons, which today are usually wax coated or over-wrapped with waxed paper, are expected to be the next major areas of penetration in the United States.

In 1960, use of this material was negligible. Now, more than 4,500 metric tons go into the coating of automotive carpets in the United States. But the big potential is in rotational moulding. This process permits large parts, or small production runs of small parts, to be made more economically with powdered resin than with either blow or injection moulding of conventional resin. Total use of powdered polyethylene is expected to double in the United States in 1964.

Exciting things also are happening in wire and cable coating where polyethylene usage in the United States alone has risen 50 per cent in two years. Submarine cable, telephone exchange and missile cable are potentially huge markets for polyethylene insulation. Particularly promising is the area of two-inch diameter cable.

A trend that should be noted here is that polvethylene is closing in on polyvinyl chloride as the world champion plastic raw material. Polyethylene took over the leadership in the United States in 1958 and in the United Kingdom last year. In Japan, where vinyl was once clearly dominant, the country's rapidly rising economy has spurred more polyethyles production, and the competition between these two plastics is now in good balance.

Low-density polyethylene, of course, also faces strong competition in many applications from members of its own polyolefin family; high-density polyethylene, and polypropylene. Among these markets are film, moulded containers, toys, houseware and automotive parts. Stated very briefly, high-density polyethylene, compared with low-density, offers greater stiffness, higher softening point and greater tensile strength. Low-density polyethylene offers higher impact strength, better low-temperature properties, better flexibility, heat sealability and lower cost.

Polypropyleae is even lighter in weight than the two polyethylenes, has greater high-temperature properties, rigidity, clarity, flex-strength and abrasion resistance. However, low-temperature brittleness has so far proved a major drawback to commercial acceptance of polypropylene for many moulded and extruded products which otherwise would be ideal applications.

Both polypropylene and high-density polyethylene are today priced somewhat higher than low-density polyethylene, but their main arcas of use are applications for which a premium price can manded — bleach and detergent bottles, cordage and textiles for example.

Potential resin manufacturers should remember that for many applications, the resin cost is often secondary to the material's performance properties. If the material fails in service, comparative production economies between one plastic raw material and another become meaningless.

The key to what the future holds for low-density polychylene rests in the fact that the seven leading countries in production of this plastic comprise only about one-fourth of the world's people, so there is still ample room for expansion of the industry. Whether or not a country should begin its own production source can only be determined by a close scrutiny of the economics involved.

Many questions have to be answered, such as: What kind of resources are available to build and equip the plant? What raw materials are available? How much end-use potential is there inside the nation's borders? Does the country have the people to provide adequate research and production performance? What technology would be most suitable for the existing and projected market requirements?

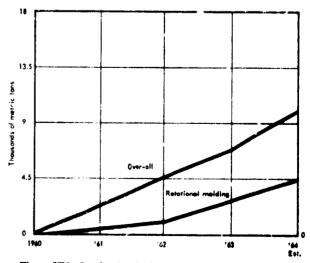


Figure XV. Powdered polyethylene use in the United States

High-densicy polyethylene	Low-density polyethylene	Polypropylene
Stiffness High softening point Tensile strength	Impact strength Low-temperature properties Flexibility Heat scalability Cost	Light weight Highest softening point Rigidity Clarity Flex strength Abrasion resistance

TABLE 3. AUVANTAGES OF LEADING POLYOLEFIN PLASTICS

Per capita consumption is an excellent guide to the feasibility of a plant. Either population or per capita consumption has to be high if a polyethylene plant is to pay its keep in a company. In other words one has to have a strong internal market for a home-bred product. Exports of polyethylene, as an earner of foreign exchange, are steadily becoming more difficult as each country attempts to become self-sufficient in meeting its requirements of plastic resins.

A country considering the starting up of a plastics industry can take encouragement from what has been said earlier about Japan, the Federal Republic of Germany, Italy and France. Eight years ago, they were in the same situation as far as low-density polyethylene was concerned. They were starting from almost nothing.

But, in every case, the potential was there and the opportunity for high *per capita* consumption was there. The energy, foresight and ability of the national leaders and the dynamism and performance of the product and the plastics industry took care of the rest. The same pattern will hold for many other countries before we reach the 1970s.

# 3. MONO AND POLYVINYL CHLORIDE

# Robert M. Brown and Harold A. Huckins, Scientific Design Company, Inc., USA

### GENERAL

The production and utilization of plastic products derived from petroleum based organic materials is an essential factor in any country, regardless of its present lev 1 of industrialization. It is perhaps even more important to the developing country as the combination of properties and applications possible through the use of plastics can in most cases prevent or forestall any need to establish a basic metal or glass industry. Also, for comparison with the conventional materials - metal, concrete, wood - organic plastics often offer economic advantages, and permit the simple expansion of fabrication industrics with a minimum of capital investment. Furthermore, organic plastics offer ranges of properties unattainable through other materials, and thus promote industrial diversification in a newly industrialized area at a rapid rate. In fact, many of the newest application developments were initiated in the less highly industrialized countries, where the need to obtain maximum utilization of materials is greatest.

There is a tremendous variety of modern plastics now finding applications in moulding -- compounds, resins, coating adhesives, fibres, films and elastomers. Many of these materials, however, have highly specialized fields of application, and are not essential during the carly phases of economic evolution. A versatile plastics industry embracing virtually the complete range of applications can be based on three primary plastics polystyrene, polyethylene and polyvinyl chloride. These materials are not only relatively low in cost, but cover the range of important properties: polystyrene for rigid materials, polyethylene for semi-rigid materials and film. and polyvinyl chloride for both flexible and rigid materials. Polyvinyl chloride is the most versatile material with property ranges that overlap those of the others. The versatility of polyvinyl chloride, its relatively low capital and operating cost requirements, together with comparatively simple production techniques, places this material in the top position for consideration in a developing country.

World-wide polyvinyl chloride sales have never declined from one yea: to another since records have been available. The latest record was set in the United States when sales in 1963 reached 1.3 billion pounds. This remarkable growth was achieved through the striking advantages of the material: excellent physical properties, the ability to be compounded to satisfy a wide range of applications, ease of processing, and relatively low cost. The potential

of the vinyl plastics, which were first introduced in 1927, did not become apparent until the Second World War. The developments made in Germany before the War were utilized in Europe and Japen when hostilities ended; in the United States, the field became wide open.

Polyvinyl chloride's array of properties include excellent water resistance, chemical resistance (resistant to most acids, salt solutions, petroleum products, fats, fungus-producing atmosphere), good strength, abrasion resistance and ease of colouring. In addition, it is one of the few thermoplastic materials that is self-extinguishing - that is, when heated enough it will melt, but will not burst into flame. When compounded, polyvinyl chloride resins can produce finished products with nearly any degree of flexibility. The rigid form of the material can be fabricated by extrusion, calendering, laminating, compression moulding, and injection moulding. The product can be machined, sawed, drilled, tapped, threaded and milled on conventional equipment. Parts can be joined by bolting, screwing, cementing, and hot gas welding.

### **APPLICATIONS**

At the present time, the bulk of polyvinyl chloride resin is used to produce flexible products, by calendering, excruding, or moulding. The popular vinyl film has found wide use for such diversified applications as draperies and curtains, yard goods, shower curtains, baby pants, rainwear and sportswear, aprons, adhesive backed film, inflatables, industrial, agricultural and automotive use. The flexible material, because of its unique self-extinguishing properties and atmospheric and chemical resistance is used for waste-paper baskets, trashcans, weather stripping, external building products, vinyl shoe soling, complete shoes, winter footwear, packaging and conveying applications, medical tubing, and blow moulded containers.

Rigid polyvinyl chloride resins are finding steadily increasing applications in the building industry. Pipe, conduit, and tubing are regular production items, and the use of polyvinyl chloride conduit has been app.oved for above ground as well as below ground installation by the United States Underwriters Laboratories. The additional good elerrical properties and heat and cold insulation properties make the material desirable for wire sheathing and insulation. Uses include insulation and jacketing for telephone cable, coaxial cable, power distribution, high voltage cable, etc. The list continues to grow. Again in the building industry, extruded product uses include window parts, doors, panels, awnings, shutters, siding, channelling. Corrugated building panels let in light while keeping out rain, wind and sun. Injection moulded applications are moulded pipe fittings, roofing, glazing, gutters, downspouts. A recent and very important new development features moulded rigid bottles, which have the important properties of glass — chemical resistance, strength and clarity. These bottles, and the transparent panels used as windows, satisfy the normal requirements for glass. Clear rigid doors for offices, banks, etc. could replace tempered plate glass.

Polyvinyl chloride resins can even be used to produce a woven fabric coating, suitable for luggage, tarpaulins, shade cloth, upholstcry.

#### NEWLY INDUSTRIALIZED AND DEVELOPING COUNTRIES

The leading producers of plastics — United States, Western Europe, Japan — comprise only about onequarter of the world population. With increasing economic growth and demand for consumer products, the remaining three-quarters of the peoples of the world will exert unprecedented demands on plastics production. Plastics industries are being introduced in some other countries including, Australia, Brazil, India, Israel, Spain and South Africa. Other countries in Africa, Central and most of South America, most of Asia, and parts of Europe are still dependent on imports of materials and technology. The small manufacturers have always been interested in plastics, because of the high ratio of annual sales to capital — as high as 10 to 1.

*Per capita* consumption of plastics in 1962, with polyvinyl chloride the leading variety, ranged from 7.7 kg per person in Japan, to 18.1 kg per person in the United States and the Federal Republic of Germany. At the same time, plastics materials accounted for from 7.4 kg per \$1,000 of national income in the United States to 20.8 kg per \$1,000 of national income in Japan.

Japan has built up a huge polyvinyl chloride industry in a short span of years. Present production applications include: rigid corrugated sheet, transparent corrugated building panels for windows, partitions, etc., extruded pipe — up to 18 inches diameter, moulded telephone sets, blown bottles; film and sheet for packaging everything but food; clear rigid doors; pipe --- for waterworks, irrigation, spraying chemicals, drainage; injection moulded parts for electrical appliances, television and radio sets, etc.

Builders in the Federal Republic of Germany, Italy, and the Netherlands also welcome the availability of plastics materials, and building codes have been drawn more liberally than those existing in many parts of the United States.

Many plastic houses and apartments now exist in almost every European country, and USSR produces small portable plastic houses. In Belgium, houses are built around a frame made of polyvinyl chloride pipe filled with concrete, and the plastic represents 65 per cent of the total cost.

### **POLYVINYL CILLORIDE RESINS**

Polyvinyl chloride usually is defined as the homopolymer of vinyl chloride, and accounts for the largest portion of the monomer consumed. Vinvl chloride copolymers for special applications can also be produced; these are polymerized combinations of vinyl chloride and other monomers such as vinyl acetate, vinylidine chloride, vinyl ethers. Usually the secondary comonomer represents less than 20 per cent of the copolymer formed. For example, the popular vinyl acetate -- vinyl chloride copolymers used extensively for phonograph records, consist of 8 to 15 per cent of vinyl acetate. Terpolymers of vinyl chloride with vinyl acetate and acrylonitrile give products which are used as fibres.

Vinyl chloride, its polymer and copolymers are materials which must be synthetically produced. Vinyl chloride is a colourless, clear, non-corrosive liquid which boils at minus 12°C and therefore must be kept refrigerated or stored under pressure. It does not readily auto-polymerize, yet polymerization is not a difficult process. Polyvinyl chloride can be looked upon as a long chain consisting of thousands of links of vinyl chloride. It is produced as a white powder similar to flour, or a white granular material finer than sugar, depending on the process used.

#### RAW MATERIALS

Production of vinyl chloride is essentially a story of raw material availability and economics, while the polymerization processes are fewer and simpler. The raw materials needed for vinyl chloride are acetylene or ethylene and chlorine or hydrogen chloride. The acetylene may also be coal or petroleum based; the ethylene from petroleum or agricultural based ethyl alcohol; the chlorine source available as a by-product from some other process or manufactured.

#### **PRODUCTION OF VINYL CITLORIDE**

There are really only three basic routes to vinyl chloride production and all the methods used are either mechanical or process variations.

One coute is the addition of hydrogen chloride to acetylene:

The second route is the direct chlorination of ethylene followed by dehydrochlorination or cracking of the dichloroethane:

The third route is the oxychlorination (really oxyhydrochlorination) of ethylene followed by cracking:

H H H H H  

$$| | |$$
  
2C ··· C · 4HCl + O<sub>2</sub> → 2 Cl ··· C ·· C Cl + 2H<sub>2</sub>O  
 $| | |$   
H H H H H

For many years, the acetylene route dominated the production of vinyl chloride. However, as ethylene technology advanced, resulting in increased production and reduced cost, interest arose in the use of this cheaper raw material. The same technology used in the pyrolysis or cracking furnaces to produce ethylene was applied to the cracking of dichloroethane producing vinyl chloride and anhydrous hydrogen chloride. This technique eliminated the wasting of caustic and hydrogen chloride and thus made the process viable. Today, about 50 per cent of the vinyl chloride is produced by cracking of dichloroethane, and most new plants use this route in the United States. Monsanto has facilities for all three process routes, using one or more depending on current material logistics.

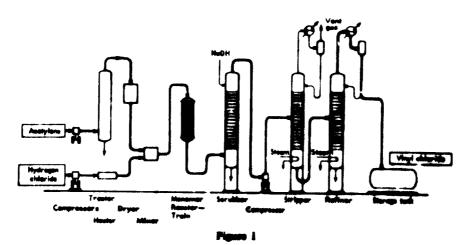
# 1. Hydrochlorination of acetylene

This classical route to MVC was the initial avenue to large-scale production and even today more monomer is synthesized by this route than any other. In the early years, the acetylene was derived exclusively from coalbased calcium carbide. In the United States, Monsanto became the first producer to employ acetylene derived from natural gas/petroleum based feedstock for the production of vinyl chloride. Since that time and especially in the last five years, most new installations have obtained their acetylene from petroleum feedstocks. This transition is likely to increase for developed countries and to a greater extent for developing nations since acetylene produced from petroleum can be less expensive than that produced from coal in large plants or where the off gases can be utilized in other processes such as methanol production.

Hydrogen chloride (HCI) has been obtained from the classical salt cake reaction of sult and sulfuric acid in a Mannheim furnace. This source of HCI is only economic where there is a demand for the salt cake, and Morton Salt uses this procedure to supply Monochem (U.S. Rubber and Borden Chemical) in the United States for their installation which was built only three years ago. In some instances, HCI is derived from the burning of hydrogen and chlorine gas. Usually, the hydrogen is derived as a by-product from caustic/chlorine electrolytic cells, but in some cases it is obtained by the cracking of hydrocarbon feedstocks such as propane or as a by-product of petroleum refining. A large part of the HCI requirements are met by the use of by-product material from chlorination units which produce such materials as solvents, refrigerants, insecticides, etc. In fact, much impetus to produce MVC by the acetylene route has come from the desire to "sponge up" the large quantities of byproduct HC1 resulting from various chlorination reactions. In the near future additional large quantities of by-product HCI will also become available from a number of linear alcohol detergent feedstock plants that are now under construction to satisfy biodegradable detergent requirements in several sectors of the world.

Figure 1 indicates one of the possible variations of the vapour phase hydrochlorination route to produce vinyl chloride and is the one generally used by Scientific Design Company in plants designed for such clients as General Tire and Rubber and Diamond Alkali.

Briefly, this process is carried out in a vapour phase tubular reactor train at a pressure of less than one kilo gauge and a temperature of 100-180°C, utilizing mercuric chloride on a carbon catalyst support. If mecessary, the incoming acetylene is compressed, treated and dried. Likewise, if required, the HCl is compressed and then is mixed with the acetylene. The mixed gases pass through the reactor train where the temperature is controlled by a heat transfer medium. Since the reaction is exothermic but must be at a minimum temperature to start, either



heating or cooling can be achieved by the heat transfer medium. The reactor effluent is scrubbed with caustic to remove traces of unreacted HC1 and the crude MVC is then compressed and passes through two distillation columns to remove first the light and then the heavy ends from the MVC product. When relatively pure HC1 and acetylene such as its usually available in the United States, Europe or Japan are used, there is little or no problem with recycle or tail gas streams, which contain an appreciable quantity of acetylene.

An alternate scheme is the use of a low conversion reactor with a large recycle system to obtain utilization of the HC1 and acetylene. This system has less investment in reactor capacity and catalyst than the previously described one, but has increased capital in recycle and additional separation equipment.

Another alternate is to utilize atmospheric purification which requires refrigeration equipment and additional scrubbing to prevent water from freezing in the distillation columns and condensers.

Each system has its own advantages and disadvantages but the economic superiority of one over the other is rather small on an over-all basis. Scientific Design has found the first-described routs to be lower in capital investment than the others and this can be of real economic importance for smaller plants in which the effect of capital charge, is more pronounced.

#### 2. Chlorination of ethylene followed by pyrolysis

The impetus for this route to MVC came instally from the desire to utilize the large quantities of dishloroethane (EDC) available as a by-product from ethylene onide production by the chlorohydrin route. In recent years steadify declining arrounts of EDC have been available from this source because the more commercially attractive direct exidation process has replaced the chlorohydria one. As a recult a very large percentage of the BCD produced today is by the direct addition of ablering to ethylene.

There are several sources of ethylene which might be considered for MVC production. One of interest to agricultural countries is the dehydration of ethyl alcohol -y entalytic means. Scientific Design offers a present for this route but does not recommend its use unless low cost alcohol is available or no other source of ethylene can be obtained.

Further sources of ethylene have been from onthe oven ans and from rolmory streams. Bibytone from such a source can be important for a MVC operation even though not sufficient in quantity for other uses. In American Che-mical Co.'s (Stauffor Chem. and Richfold Oll) plant in Southern California, an othens-othylene minture from Richfield's refinery is separated, the other ine di ioria at and the otherse returned to the refinery for fust use. As domand for ethylene increases, Biolodicid will creak the othens. Reservery from onto even gas has be particularly in Barrage where the conditions f from refinery strength have been has former ne utilized ing for recovery m have been hen forestable than in ary staats the United B o. Due to the anime and variety of the vertexes impressibles and also to the low out

of ethylene recovery from this origin is rather difficult and often uneconomic

Of most interest today is the nv slysis or cracking of petroleum feedstocks. In spite of the decreasing cost of ethylene and the availability of FDC, the production of vinyl chloride by the cracking route has been somewhat slow to take hold. This phenominion is due largely to the fact that EDC cracking produces approximately 0.6 kilos of HCT per kilo of MVC manufactured often creating a disposal problem. Further, while this process can be very attractive on a large scale, the capital investment is higher for smaller installations as compared to the acetylene route. In iddition, the cracking of FDX while similar to that used for ethylene production is tricky in its own right which held up development of the technique.

Figure II indicates the FIM cracking route to vinyi chloride starting with ethylene and chlorine. Untilizing purchased FIX would of course eliminate the FIX rouctor but the purification columns preceding the pyrolysis unit would be required for handling the recycle streams although they could be reduced somewhat in size

In this process, ethylene and chlorine gases are charged to a reactor system containing catalyst and liquid FDC which acts as a solvent for the feed gases. The reaction is rapid and goes essentially to completion with the formation of only a small amount of hy-products primarily higher phlorinated compounds. The two distills ion oblumns remove light and heavy fractions from the crude EDC along with repurification of recycle streams from the MVC portion of the plant. The purified EDC is then partially oracked at high temperature in direct fired furnaces to yield a crude mixture containing principally hydrogen phloride, MVC and unreacted EDC. The amount of EDC crucked is limited to 40. 30 per cent per pass and the over-all yield is lower as the conversion is inversed.

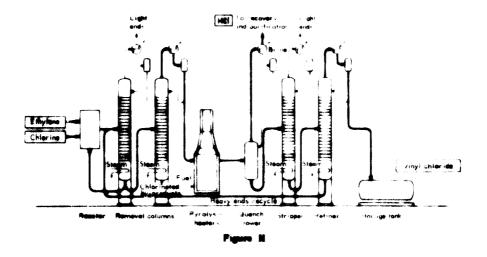
In order to obtain maximum recovery of the desired product, the gases from the oracking unit are quonohed rapidly. The anhydrous hydrogen oblevide by-product is piped away from the unit and further handling depends upon the end use. Some applications require no further treatment whereas others may call for adsorption desorption in water to obtain a very pure product. Liquid anashed products are refined in a distillation train to remove light and heavy ends the latter consisting primarily of unresoled EDC with some higher oblevinated products formed in the pyrolysis, which is recycled to the EDC purification columns to recover this raw material.

During the past five to ten years many MVC producers in the United States, ilurope and Japan have begun to utilize sense variation of the BDC route. Even fairly small plants are starting to adopt this veheme ... Electroobseniaal Industries in Israel and Grace Chemical in Pers.

#### 3. Onychlaringsion of orlyisms and hydrogen chievide

In recent years, there has been intrice research to devedage a present to produce visual chaotide directly from ethylane and couples hydrogen chieveds.

19



Theoretionily, it is possible to produce MVC as indiunted by the following over-all equation

This type of reaction has become known as onychlorination even though this designation is not strictly correct. As can be seen, total utilization of the hydrogen chloride is accomplicated and the only products are MVC and water

The one step process has not reached commercial realization because of poor conversion per pass, poor yield due to by-product formation, difficulty in super-sting and recycling raw materials, correction, and poor establyst Mb. While it is desirable to use air increased of oxygen because of the cost saving, air increases many of these problems.

By use of a two step process, many of the difficulties have been removed or at least distinuted. In this process, EDC is first formed by enychlorization. Then, ecorestional pyrolysis is used to produce MVC and hydrogen obloride which is recycled to the onychlorization with. The over-all EDC equation is

The enjolutiontion reaction is a modelization of the old Denson process in that actually the hydrogen obtaction is converted into water and obtactor which then reacts with the otherhone. Obvicularly, could a process requires a rapping of hydrogen obtaction which in many cases is sugglied from accordingtonal EDC pyrolysis. This spatem would then utilize otherhone and obta-rise to gendues vispi obtaction with no residual hydrogen obtaction.

The production of BDC by expeditorization is a respect phase reaction carried out usually in the maps of 380 to 489°C depending upon the particular process scheme and establyst. Catalysts consist of materials such as copper chloride utilizing various supports including alumina, earbon and caloimed Pullar's earth.

While much work by many companies has been performed in the field of enychlorization, relatively listle information is available as to the real investment and operating costs since only a few commercial plants exist. In the United States, Monsanto and Dow we using this route, and Goodrich Chemical is now operating a 400 million Ib. vinyl obteride plant, the largest such unit. Several other plants are in construction or have been approaced

Because of its ability to use otherious which beaucely is less supervive then acetylens and because by-product hydrogen obleride is oliminated, the enychlorination present to produce MPVC is of considerable importance and as more experience a gained will probably become even more experience a gained will probably become even more attractive where these factors are of prime significance.

# 4. Combined facilities — observation of objects plus hydrochloringsion of avoidence

As indicated proviously one of the major prob with the BDC erastaing route has been the di of the be-area hast hydro n dii én. In i ies, the hydrogen ablevide has been dis a nant amba in ness the product cost due to the h stained in the hydrogen d **-**-has these is as lly a dia casi cost (housing to say, as n, etc.). In other ensue, the by b has been sold in aqueous form for oil well t nt, start pishilan, etc. Gua ly, however, these or its and just as the as re ant hime and nd as a "spage" for the by-good to base utili 5 A **, .** n annd im anns a with BDC and ا ي و

The first combined plants of this type resulted when emining antylene MPC plants obtained their SECI

requirements from a newly installed parallel EDC unit. The by-product hydrogen chloride can be used directly in the acetylene process with no further treatment. Obviously, the capital requirements of such a plant are fairly high, but can be reduced by utilizing common vinvi chioride purification facilities. If such a complex is contemplated for the future, a relatively small extra investment can be made initially in the purification facilities to handle such an expansion. Fortunately, though desirable, it is not necessary to have the acetylene and ethylene available at the same location since EDC can be produced at one site and shipped to the acetylene location. In general, because of the dual reaction systems, such a combination plant tends to be limited to only large installations of 50,000 metric tons or more per year. The major exception to this is in the case of expansion

Many of the MVC producers who utilize the EDC cracking route do have the dual acetylene-ethylene systems. Among these producers are Monsanto, Dow and Goodrich in the United States, ICI and Dritish Geon in the United Kingdom, Pechi in France and DASF in the Federal Republic of Germany.

As a variation on the EDC route, it should be noted that Ethyl Corp. and others use the by-product hydrogen chloride by reacting further with ethylene to produce ethyl chloride in Ethyl's case, the ethyl chloride along with some EDC is used in the production of tetraethyl lead which makes a very attractive total package. The markets for ethyl chloride are rather specialized and in most locations would not be commercially attractive

#### 5 Combined hydrochlorination/chlorination utilizing a dilute acetyline/othyline\_food

In the conventional processes for producing othylans and apotylone, recovery ned purification are a most significant item in the cost of production. To avoid this expenditure, a number of organizations including Kuroka Chemical in Japan and SBA (Société belge de l'anote et des produits chamaques du Marly) in Belgium have developed a presses, which feeds a combined dilute stream of these two hydrocarbons to a series of reastors and separating-recovery columns. Kurche has announced the successful startup of such a plant. The hydrocarbons are obtained by the partial exidence of naphtha using high purity exygen to give an equal molar ratio of the red hydrocarbons at about 30 per cent wt. yield. The total content of CpH<sub>2</sub> + CpH<sub>4</sub> in the erashed games is about 20 per cent with the bulance as hydrogen, ma corbon mononids, carbon dionido and tree n of his hydrocarbons. The officiant is first quanched and th sorubbed to remove the earliest and tarry compati nin. The game are compressed and the higher hydrocarbons are removed by solvest sorubbins.

The associations is selectively recented with HC1 using a construct conductions to prevent the eccavarians of othermous to othermous dashborids. The construct minimum is then could be a solvent corrup towar where the MFVC is removed, while the construct betterns are could to a distilation system for MFVC gravitanties. Chieving is that added to overhead gases and it reacts with the ethylene in a liquid phase reactor consisting of EDC with a ferric chloride catalyst. The EDC effluent is purified by distillation and cracked in a conventional manner as described previously. The HC1 is recycled back to the first reactor while the MVC produced is purified along with that produced from the acetylene.

From this description, it can be seen that this process has all the steps of the combined chlorination-hydrochlorination process except that the reactors are in series rather than in parallel and they are handling dilute gases. **Because** of inherent complexity of this process and the fact that it requires an independent acetylene-othylene unit dedicated to the vinyl chloride plant, the process will probably only be of limited usefulness to fit a special and particular set of economics essentially of greater interest for a large size plant (approximately 50,000 metric tons per year or larger) where no other needs for acetyleneothylene exists. Even at this capacity level, the size of hydrocarbon feedstock plant is small by comparison with modern ethylene units, so that the savings in processing dilute hydrocarbons might be negated. The usefulness of this process is also substantially improved if the off-gas can be used as a synthesis gas which is quite possible.

#### ECONOMIC FACTORS

In order to permit an assessment of the most desirable route to follow for the manufacture of MVC, the following economic factors should be considered

#### A. Hydrocarbon supply

1 Ethylene. The over-all economics of ethylene manufacture is a most complex subject and is a topic of a separate report at this conference. This versatile building block can be produced from a wide variety of hydrocarbon feedstocks such as refinery light gases or condensate from partial liquidification of natural gas all the way to heavy petroleum fractions. The price range of ethylene in industrially advanced countries varies between 3.3-12.1¢ per kile. Some big new units now being completed in the United States can possibly result in lower prices, such as 6.6¢ per kile, but of course, this situation would not apply for industrially emerging countries. In some areas of the world, ethanol might be a suitable initial feedeteek and can provide an agricultural base for onl industry during the transition period in unindustrialized countries.

2. Acceptione. It takes approximately 0.45 pounds of acceptions and 0.62 pounds of HC1 to make a pound of visyt chlorids. In virtually all cases, acception is more expansive than ethyless. Its price range in industrially advanced countries is between 18.7-26.4¢ per hile. At an earlier era, this reactive chemical was based upon earlied. The calatium earlide routs is often an attractive selection under these conditions, as capital investment is law for conversion of earlide to acetylens. How acetylens plasts is industrially advanced countries, petroleum-based fundatesche is the preferred route for large plants.

#### B. Halogen supply

1. Chlorine. The current price of chlorine in industrially advanced countries is 5.5 - 7.7e per kilo with a price being established by cost of electric power and sales of chlorine and caustic. This is also a complex subject. Often, in under-developed countries, caustic is of greater usefulness than chlorine, thus offering opportunity for lower priced chlorine.

2. Hydrogen chloride. The price of this material can vary from 4.4¢ per kilo to a negative value up to 1.1¢ per kilo, where it is such a disposal problem that it must be neutralized. Price is established by these economic marketing factors. The higher price is usually the result of producing HC1 by chlorine burning.

#### C. Plant size

1. The exact minimum plant size varies from country to country, depending upon local marketing conditions and government policy concerning protective tariffs. In any case, a 10 million pound a year plant is probably the smallest that should be considered in any location. In industrially advanced countries, at the present time, 100 to 200 million pound plant capacity is the usual "conomic minimum size.

In order of increasing capital investment requirements, the various processes are arranged as follows: 1. acetylene plus HC1; 2. ethylene plus chlorine to EDC-MVC; 3. combination 1 and 2; 4. oxy-chlorination plus 2; 5. dilu: acetylene plus ethylene combined process.

#### PROCEES SELECTION

Unless it is economically feasible to scrap a process in three or four years because of some special situation, the choice of a process to produce vinyl chloride should fit into a long-range programme.

Let us consider a possible programme where ethyl alcohol is readily available from agricultural sources at reasonable prices.

Initially, ethylene would be produced from the alcohol, chlorinated to EDC and then vinyl chloride obtained by pyrolysis. The by-product hydrogen chloride could be sold as muriatic acid or neutralized with limestone and discarded. As other uses for ethylene developed, the alcohol route could be abandoned and ethylene produced by cracking or purchased. The chlorination and EDC cracking units would still be utilized. As need for more vinyl chloride arose, production could be nearly doubled by using the by-product hydrogen chloride from the existing unit along with ethylene in an oxychlorination unit. This last stop would require additional EDC cracking units but the original installation would remain in use. Also, expanded vinyl chloride purification equipment would be required to handle the extra load unless this was provided for in the initial installation. A programme her to this was adopted by W. R. Grace for Peru but before it could be put into effect, the chlorine supply situation changed and they are proceeding with the exychlorination stop simultaneously with the aleshol, ethylene, EDC and cracking routes outlined above. Whether ethylene from petroleum eventually will be used depends upon future developments.

Electrochemical Industries in Israel chose another course. They utilized coal based acetylene for approximately three years and are now converting over to the use of ethylene which necessitates the scrapping of some of the acetylene-based plant. It may be that at a future date Electrochemical plans to use a combined ethylene/ acetylene route and salvage the original installation.

These are but some examples of the type of growth planning which have been experienced. Other schemes might include importation of either EDC or vinyl chloride until such time as an installation could be economically justified.

It should be pointed out that it is not necessary to have individual vinyl chloride plants for each PVC plant and if transportation is available, one vinyl chloride plant can supply several polymer plants thus realizing the savings attendant to a larger installation. In the United States, there are several merchant suppliers of vinyl chloride who sell to the various PVC producers as well as companies who provide monomer from one location to several branches. For example Ethyl Corp. supplies monomer to Firestone in Pennsylvania and Atlantic Tubing in Rhode Island as well as others while Goodrich in Calvert City supplies its plants in New York State, Ohio and Kentucky.

#### POLYVINYL CHLORIDE

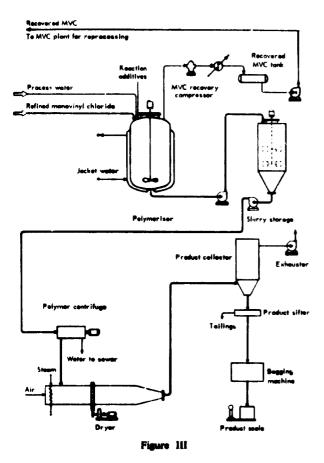
The polymerization of vinyl chloride to form PVC is represented chemically as:

$$\begin{array}{c} H \quad H \\ \downarrow \\ X C = C \\ \downarrow \\ H \\ C \end{array} \rightarrow \begin{pmatrix} H \quad H \\ \downarrow \\ -C - C - C \\ \downarrow \\ H \\ C \end{matrix} \right) X$$

There are three basic polymerization routes to the production of PVC resins: 1. *in situ*; 2. emulsion; 3. suspension.

There are, of course, variations on each of these, but for the most part we will discuss primarily the three basic types. The *in situ* method consists of polymerizing vinyl chloride in vinyl chloride, but since vinyl chloride is not a solvent for the polymer, it is necessary to stop the polymerization at approximately 60 per cent or less conversion, usually by releasing the volatile vinyl chloride from the reaction leaving the solid polymer behind. There are two processes using this technique today, both of which are relatively high in both investment and operating cost and one of which produces considerable quantities of low quality by-product resin. For many years now neither of these processes has been expanded and there is little likelihood of their being considered for today's markets.

The suspension technique is really a block polymerization in which small droplets of vinyl chloride are polymerized in a water suspending agent. A true block polymerination in which monomer is polymerized in a mould



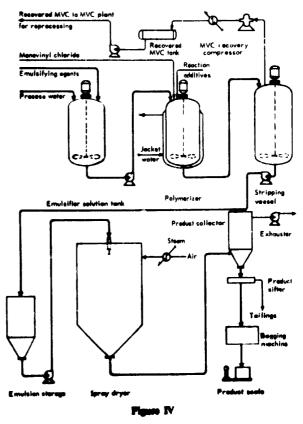
cannot be utilized because the heat of reaction partially destroys the polymer. The suspension technique allows the dissipation of this heat in the suspending medium. Because of the nature of the suspension system very few chemicals are used in the polymerization (only small amounts of catalyst and suspending agents) which results in a polymer of very high purity. The capital investment for such a plant is the lowest of the three basic techniques and because of the small amount of chemicals used, as well as the fact that the majority of the water can be removed by centrifuging before drying, the production costs are also the lowest. The products from the suspension process are used for the great bulk of applications in the United States including film, shoeting, wire insulation, hoses, as well as rigid sheeting, extrusions and blow moulding. Further, this process lends itself readily to the production of copolymers which are used for special applications such as floor tile and phonograph records. The popular vinyl acetate-vinyl chloride copolymers are produced with a minimum of additional equipment which includes simple storage tanks, transfer pumps and metering facilities.

In the suspension process, pure process water is charged to the polymerizer by pumping, followed by the catalyst and other chemicals. The MVC is also pumped into one of several reactors and with the agitation on, the contents are brought to reaction temperature by means of hot water in the jacket. Once reaction starts, besting stops and cooling water is applied as needed. Reaction continues to approximately 90 per cent conversion whereupon the residual MVC is recovered by means of a compressor. The recovered monomer is condensed and returned to the MVC plant for purification. If the MVC plant is remote from the PVC plant, many installations have a small distillation column to handle the recovered MVC.

The polymer in the reactor now is in the form of small granules suspended in water. This slurry is pumped to agitated storage tanks from which it is fed to a centrifuge. Here, most of the water is removed leaving a wet filter cake which has the consistency of wet sand. Drying is accomplished by passing the polymer concurrently through a rotary dryer with heated air. The same air used for drying conveys the product to a bag collector and the clean air is discharged to the atmosphere through a blower. The PVC passes by gravity through a sifter to remove oversize material and is packaged, usually in 25 kilo paper bags.

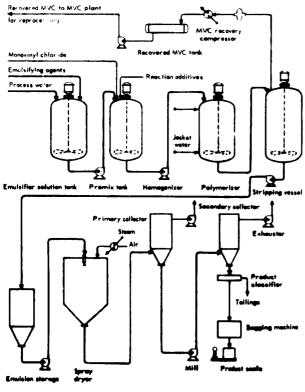
Where demand is great enough and transportation facilities available, bulk storage is installed in addition to the bagging facilities. The bulk product is then shipped by hopper truck or railroad car or in the case of bags, on pallets.

The emulsion polymerization technique, which has been used quite widely because it was a natural outgrowth of the emulsion polymer technique used in the synthetic rubber industry, consists of polymerization of an emulsion of vinyl chloride and water. The vinyl



chloride to water ratio could vary widely, but usually does not exceed 40 per cent of the total mixture. The emulsion process has one advantage over the others in that continuous polymerization can be fairly readily utilized. Also, because of the nature of the polymerization the emulsion process can produce certain end-products which are very difficult or impossible to produce by other techniques. These products are usually specialty products and command a premium in the market place such as plastisol type resins. Except for the specialty applications the emulsion process has a distinct disadvantage in producing general purpose resins because of the impurities introduced in the form of relatively large amounts of emulsifying agents. Further, the cost of such chemicals, along with spray drying to obtain the final product, results in increased cost of production. The impurities mentioned reduce the chemical resistance, the electrical resistivity and ultra-violet resistance of the end-products, as well as increase water absorption. In addition these impurities often cause trouble in compounding because of incompatibility with dyes and other compounding chemicals.

In the emulsion process, the emulsifying agents are dissolved in the process water which is then charged to the polymerizer by pumping. Because an emulsion (similar to milk) is formed which foams readily, recovery of the unreacted MVC is performed in a stripping vessel. This stripper is much larger than the polymerizer in order to handle the foam. As before, the recovered monomer is returned for purification.





The stripped emulsion is transferred to storage tanks from which it is pumped to a spray dryer where all the water is removed by hot air. Again, the drying air is used to convey the product to a collector. At this point the PVC is in the form of a fine powder, and sifting must be performed by a brushed screen. The polymer is bagged as before.

Sometimes special emulsions or latices are sold without spray drying and are drummed for use in dip-coating applications. Much care must be used to prevent coagulation of the latex or a useless product will result.

In order to produce a plastisol polymer, an ultra-fine (1 to 2 microns) product is usually required. This is accomplished by adding more equipment and steps to the emulsion process. In this process, the emulsifier solution, catalyst and MVC are charged to a premix tank and all the ingredients are intimately mixed by means of a mechanical homogenizer. The resulting mixture is charged to the polymerizers and reaction takes place as in the previous case. MVC recovery, storage, drying and product collection are the same as for regular emulsion. A new step is now introduced to ensure the desired fine particle size. This is accomplished in a mill which breaks up any agglomerates formed in drying. Milling does not grind the PVC particles as they are too soft to shatter. The product from the mill is air conveyed to a secondary collector and instead of sifting, an air classifier is usually used to separate oversized material. Air separation removes the coarse particles but also removes a fair amount of satisfactory material (10 to 20 per cent) and often additional equipment is added for separate screening and recycling of the oversize material in order to reduce losses. As before, the finished product is packaged in 25 kilo paper bags and stored on pallets.

As can be seen by comparing the above descriptions, the emulsion process requires more capital and more rigorous operations which increase product cost.

A developing nation should first install a suspension polymerization plant. One of the chief attractions for plastisol resin made by the emulsion process is that it can be converted to end products with minimal capital investment. However, this simplicity of application can easily lead to a poor decision if the future potential of this product is not properly evaluated. Low application investment cost is thus obtained at the expense of high priced raw material. Looking to the future, such techniques as calendering film, expensive though they may be initially, are the areas where the greatest growth potential is to be realized and where the suspension process dominates. The differential cost between a suspension and a plastisol plant would go a long way toward installing a calendering operation and the application of this money toward this end might well be considered.

Economic factors. Basically, all the processes for producing PVC are batch processes which is true even in the case of continuous emulsion polymerization where batch-type reactors are interconnected. Because of the batch nature it is possible for relatively small plants to compete with large installations. For instance, the differential production cost between a 5,000 metric ton/yr. plant and a 20,000 metric ton/yr. suspension PVC plant may be of the order of 3¢/kilo. This is an appreciable amount if the two plants were in close proximity, but since we are presumably discussing plants in separate countries, when freight and duties are applied, this differential may disappear entirely.

In the range of 5,000 to 20,000 metric tons per year, the capital investment for a suspension PVC plant varies from 2.5 to 4e per kilo. A standard emulsion plant might be 15 per cent more while a plastisol plant could run 30 per cent additional. Since demand for emulsion and plastisol products is relatively small and the corresponding plants are usually small, the investment costs run on the higher end of the range.

As in vinyl chloride production, the main factor in production cost is the cost of the raw material — in this case, vinyl chloride. Since this runs 60 to 75 per cent while capital investment's direct share is only 6 to 10 per cent, capital changes have a lesser effect upon the cost of production. Nevertheless, since the PVC market place is very competitive, every tenth of a cent counts and cannot be completely ignored.

The cost of production for the emulsion process can be as much as 20 per cent over that for suspension PVC, especially in the case of plastisol polymers. This differential, of course, is due in part to the investment cost and also to more expensive chemical and operating components. In both types of processes it is possible to prepare for future demand by installing larger auxiliary equipment initially (such as centrifuge, dryer or spray dryer) and then adding additional polymerization reactors at a later date. This, of course, imposes some burden on the already burdened small plants, but should definitely have a payout in the future since the history of growth in PVC has resulted in every single producer enlarging his operation eventually by the duplication of existing equipment.

Because of the batch nature of the PVC plants, labour costs remain fairly linear, but some reduction is experienced in size. A foreman is required on each shift but one foreman can handle either a 5,000 or a 20,000 metric ton per year plant. A 5,000 metric ton/yr. plant would require 3 operators and a foreman per shift plus a day utility operator while a 20,000 metric ton/yr. olant would require approximately 9 operators and a foreman per shift. This seems to disagree with the previous statement about labour being linear, but this is due to a disproportionate situation in the smaller plant. A 30,000 metric ton plant would be almost directly proportional to the 20,000 metric ton plant. These labour figures do not include maintenance or shipping men, and assume all the product is bagged. Bulk handling and shipping would reduce these figures by one or two men a shift in the larger plant, but this saving could not be experienced in the smaller one.

#### SUMMARY

Because of its wide range of applications and continuing growth, PVC should be a keystone in any chemical development programme. In planning a new installation. provision for the future should be incorporated; if not by purposely oversizing the initial plant or portions thereof (such as the drying end), at least by making provision in the layout for the expansion so that any operating savings possible may be realized. Every producer of PVC in the world has been expanding at such a rate that in the United States alone three new producers who started in the business in 1956 with 5,000 metric tons per year plants have each at least guadrupled production. In fact, one enlarged eightfold and the other two will reach this level shortly. These producers are Pantasote, Borden and Thompson. Again in 1957 two more joined the industry and each has enlarged from 5,000 metric tons to over 30,000 metric tons per year (Cary and Atlantic Tubing). Similar expansion has been occurring in country after country - Japan, Italy, China (Taiwan), etc.

It should be noted that all of the above-named plants were initially suspension type plants. While some emulsion facilities have been added, over 90 per cent of the product in these enlarged plants is suspension-type PVC.

It has been and remains our recommendation to new producers entering the PVC field to start in the suspension field. Then, when fully established, production can be broadened by adding emulsion facilities if the market demands warrant.

On the other hand, since copolymers can be produced with only a very modest increase in investment (approximately 5 per cent), this expenditure should be made with the initial plant. Co-monomers such as vinyl acetate would be purchased since they represent a small percentage of the copolymers -- 5-15 per cent -- which in turn represents less than 25 per cent of the total production.

It should be pointed out that several types of homo and copolymers are required by the market. These are all produced in one plant — either emulsion or suspension — using a blocked operation, which means one after the other, not simultaneously.

# 4. STYRENE RESINS FOR PETROCHEMICAL GROWTH

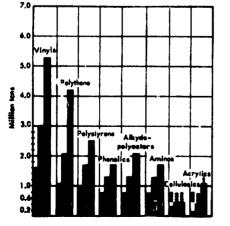
Peter W. Sherwood, Consulting Chemical Engineer, and R. G. Edmonds, The Badger Company, Inc., USA

Styrene resins are the third-largest group of plastics, following after vinyls and polyethylene. As shown in figure I, they are still in a major growth phase, and worldwide production is expected to rise from one million metric tons in 1960 to 1.8 million tons in 1965 and over 2.5 million tons by 1970. By way of comparison, consumption of vinyls should reach 5.3 million tons per year in 1970, while world output of polyethylene is foreseen at 4.2 million tons during the same year. These three groups eclipse the growth outlook for all other major classes of plastics, namely the phenolics, the alkyds and polyesters amino resins, cellulosics, and the acrylics.

Polystyrene production is today a world-wide industry — but this is a development of the last decade. As recently as 1955, only eleven countries had polystyrene manufacturing facilities and all of these were industrially advanced nations. By 1960, the number of polystyreneproducing countries had grown to 30 and, by 1965, the total number of countries engaged in this industry segment will be closer to 40.

The broad acceptance of styrene resins can be ascribed principally to low cost, processing ease, excellent transparency, and availability in an unlimited range of attractive colours. In fact, on a price-per-unit volume basis, the unmodified polymers offer the lowest cost of any thermoplastic material, excepting only a few grades of polyethylene.

The point is brought home clearly by table 1. As shown, general-purpose polystyrene with a list price of 14.5 cents



**Figure 1.** World : estimated future growth of individual plastics

TABLE 1. UNITED STATES PRICES OF MAJOR THERMOPLASTICS

	•••		, Feb. 1964)
Material	Lb/cu. inch	¢/ib.	¢/cu. Inch
Polystyrene			
General purpose	0.0383	14.5	0.56
High impact	. 0.0372-0.0375	21-32	0.79-1.19
Polyethylenc			
Low density.	0.0330-0.0339	13.5-22	0.45-0.75
High density.	0.0340-0.0346	25	0.85-0.86
PVC compound	0.0462-0.0502	15-41	0.69-2.06

per pound is available for 0.56 cents per cubic inch, a price substantially below that of most grades of polyethylene and polyvinyl chloride. It might be noted that only two other thermoplastic materials, namely styreneacrylonitrile copolymer and some of the cheaper polypropylene grades are available at less than one cent per cubic inch.

The reason for the low cost of polystyrene is to be found strictly in the low monomer cost. In all of the basic styrene resins, this is the item which accounts for 60-65 per cent of total factory cost. This is illustrated in table 2 which shows, in a generalized way, the manufacturing costs for general-purpose polystyrene. Conversion cost varies, of course, from plant to plant as well as with the scale of operation. An overall trend may, however, be discerned in this as in other industries which is leading toward more fully automated polymerization lines. The effect of this trend is an increase in investment cost and therefore in annual capital charges, which are more than offset by savings in direct labour cost.

#### TABLE 2. PRODUCTION COST OF POLYSTYRENE

Conversion Cost (incl. depreciation) Bags or fibre drums				
Monomer (at 8.5¢/1b. monomer pluz freight) Freight to deliver polymer (av.)				9.2
	•	•	•	

14.0-14.54/16.

With monomer cost making up the bulk of polystyrene costs, it becomes of interest to take a look at some of the economic and technical aspects involved in the manufacture of styrene monomer.

Upon completion of present projects, say in late 1965, world-wide capacity for styrene (excluding countries with centrally Planned economies) will be 2.4 million metric tons. This represents a 43 per cent increase over installed capacity as of late 1963. It is also significant that over 17 per cent of the world's styrene capacity will be outside the industrial centres of North America and Western Europe, though 12 of the 17 per cent are located in Japan. A break-down of capacity for styrene monomer by geographical region is shown in table 3.

Technology for the inanufacture of styrene monomer can today be readily purchased from a number of sources. For example, The Badger Company, Inc., which has during the last two years built the two largest individual production units for styrene in the world, can provide access to the combined styrene know-how of its own organization, of Union Carbide Company, and of Cosden Petroleum Company.

A key to the economics of styrene manufacture is the route taken to the production of intermediate ethyl benzene. Two basically different approaches — direct recovery from reformate and synthesis from ethylene and benzene — are available.

The direct recovery of ethyl benzene from the  $C_a$ aromatics fraction of naphtha reformate involves a highly sophisticated superfractionation process which was originally developed by Cosden Petroleum Company and The Badger Company, Inc. Because details of this approach are covered in a separate paper at this meeting, it will suffice to point out that such direct recovery is economically feasible only in conjunction with extensive reforming capacity and in conjunction with facilities for the recovery of individual xylenes. By next year, direct recovery will account for nearly ten per cent of United States' ethyl benzene capacity and for somewhat more than five per cent of world-wide capacity.

All the remaining ethyl benzene capacity is based on the alkylation of benzene by ethylene. This reaction may be promoted by a number of catalysts. Foremost in importance is the liquid-phase alkylation of benzene in the presence of anhydrous aluminium chloride. This

#### TABLE 3. 1965 CAPACITIES FOR STYRENE MONOMER (Countries with free enterprise economies)

								Capac	ky
	 Ra	<b></b>	R	 	 			(Thousand motric sons/year)	Per cen
N. America								1,230	<b>52</b> .1
Burope								725	30.7
L. America .								66	2.9
Other								339	14.3
					Te	тл	L	2,360	100.0

conversion is carried out at 90-100°C and moderate pressure. A significant asset of the process is its suitability for disproportionating polyalkyl benzenes which are formed as inevitable by-products. Ethylene and benzene values contained in these higher-boiling products can be recovered, for the most part, by re-circulation through the primary reactors. Thus, the process is capable of achieving an ethyl benzene yield in excess of 95 per cent, based on either raw material.

The use of silica-alumina catalyst in the vapour-phase ethylation of benzene calls for drastic conditions — typical pressure is 900 psi and temperature is 310°C. Compared to the much more prevalent liquid-phase alkylation process, this approach suffers from the following shortcomings: it requires a higher benzene-to-ethylene ratio; it calls for use of high pressure equipment; some butyl benzene formation occurs and separate equipment is needed to carry out the de-alkylation of by-product polyalkyl benzenes. Against this, the use of silica-alumina catalyst results in lower catalyst cost and it minimizes the waste disposal and feed pre-drying problems which are inherent in the use of aluminium chloride. Furthermore, use of silica-alumina side-steps the need for corrosion-resistant equipment.

Various other alkylation catalysts may be used. Among the more interesting, mention should be made of boron trifluoride which reportedly permits use of dilute olefin gases for the simultaneous formation of ethyl benzene and cumene. As in the case of aluminium chloride catalysis, polyalkyl benzenes can be re-cycled directly for disproportionation, and a fairly low benzene-to-ethylene ratio may be maintained. Typical operating condition is 550 psi and 120°C. Utilization of both benzene and ethylene is reportedly about 95 per cent. Indications are that high investment is required for plants of this type, especially when they are designed for use of dilute olefinic gases.

Catalysis by supported phosphoric acid or phosphates calls for the use of pressures approaching 1000 psi and requires very high benzene-to-ethylene feed ratios in order to suppress formation of polyalkyl benzenes. The process has been carried out commercially but has not found wide acceptance.

After ethyl benzene has been synthesized and purified by distillation, it is dehydrogenated to styrene. This conversion is carried out in the vapour phase. Three catalysts account for most of the world's styrene capacity: (1) Esso's 1707 which contains ferric oxide, potassium oxide, magnesium oxide and cupric oxide; (2) Shell's 105 which is iron oxide promoted with potassium carbonate and chromium oxide; and (3) zinc oxide promoted with smaller quantities of alumina and chromates. a catalyst which was originally developed in the Federal Republic of Germany.

Formation of styrene is favourably influenced by operating at low partial pressure of reactants. In universal practice, steam is therefore employed as diluent. This steam injection serves the further purposes of suppressing catalyst-fouling carbon deposition and of supplying the heat of reaction. Average reactor temperature is about 600°C with the outlet some 60-70°C below inlet temperature. Conversion efficiency is greatly affected by per-pass conversion and, thus, by space velocity. Normally, perpass conversion is held between 35 and 40 per cent, corresponding to a yield in the vicinity of 90 per cent. The reactor effluent is quenched and cooled. After separation from water, the crude product contains 37 to 40 per cent styren 2.

Styrene and ethyl benzene boil within a close range. The problem of their separation is compounded because of styrene's strong polymerization tendency at elevated temperature. To overcome these difficulties, it is necessary to carry out the fractionation at high vacuum and low hold-up time and in the presence of inhibitor. Sulfur is most commonly employed in this service. In a finishing distillation, styrene is freed of sulfur inhibitor. This final step is carried out with the addition of the storage inhibitor — normally tertiary butyl catechol — to the top plates of the finishing column.

Some twenty-five years ago, the difficulties in separating styrene from ethyl benzene nearly defeated the direct dehydrogenation route which has just been described. In fact, the oldest United States styrene plant uses a completely different route in which ethyl benzene is oxidized to acetophenone which is then hydrogenated to methyl phenyl carbinol and is finally dehydrated to styrene. Here, the purification problem is greatly simplified, but the economics are such that the process can only be justified by sales of co-produced acetophenone and methyl phenyl carbinol, both of which have a very limited market.

Earlier in this discussion, it was shown how crucially the cost of polystyrene production is influenced by the price of styrene monomer. Now that we have had an opportunity to take a brief look at the technology of styrene production, it seems, therefore, in order to get a general idea of the factory costs involved. In order to get a general idea of the factory costs involved. In order to set the scope, table 4 shows typical investment and operating costs in styrene plants rated at 20 million pounds per year. This is, of course, extremely small by American standards, but it is a plant capacity which may be realistically considered for emerging economies. It should be emphasized here that cost of producing styrene monomer drops sharply with increasing plant size.

For the present analysis, table 4 shows two types of plant. In Plant A, ethyl benzene is obtained by direct recovery from a  $C_a$  fraction of naphtha reformate. Within battery limits in the United States, this plant shows an investment cost of about \$2,900,000, or 14.5 cents per annual pound of styrene production.

In Plant B, ethyl benzene is manufactured by alkylation of benzene with ethylene. On a comparable basis, the investment cost is approximately \$2,600,000, or 13 cents per pound of annual production. It should be noted that in large, modern integrated plants this investment per pound of annual production is reduced markedly.

Production cost is calculated at a benzene price of  $21.5 \notin$  gallon and an ethylene value of  $4.8 \notin$  pound which leads to a total production cost of  $7.2 \notin$  pound styrene by the alkylation route in the small plants being discussed here.

#### TABLE 4. STYRENE MONOMER COFFE

(20,000,000 pounds per year)

			 _	 	 		 <b>P</b>		4			Plan: B
Plant type		•	•	•	•	E	iy] ec				e	Benzene alkylation
Investment			•		•		\$ 2,5	)00	),0	00		\$2.600,000
Manufacturing co	et:	L										
Raw materials.												4.1¢/1b.
Operating cost												2.2
Depreciation .												0.9
Production cost .												7.2¢/1b.

An operating cost comparison for the two types of plant shown in table 4 cannot, however, be made very meaningful for a generalized case because the value of recovered ethyl benzene as a co-product aromatic is usually fixed arbitrarily by its production cost via the alkylation process. By this method of bookkeeping any economic advantage of ethyl benzene recovery, which depends on the relative plant values for benzene, ethylene and  $C_s$  aromatics fraction, would accrue to the coproduced xylenes.

These are the processes which will account for worldwide production of well over 4.5 billion pounds styrene this year. So we should perhaps examine more closely where all this styrene goes.

Over-all end-use distribution of styrene produced in the United States can be seen from table 5. Polystyrene and other resins, notably ABS and styrene-acrylonitrile, account for some 53 per cent of the total and, within this group, the high-impact polystyrenes clearly show the fastest growth rate, having raised their share of the United States styrene market from less than 25 per cent in 1963 to the present 26.8 per cent. GR-S rubber, which once accounted for the lion's share of styrene monomer demand, today consumes only 22.9 per cent of the United States output and even this portion of the market will not be maintained. Styrene and styrenebutadiene latexes, used mainly in a variety of coatings,

#### TABLE 5. STYRENCE OUTLETS (United States, 1964 estimate)

).			•	•	•		23.6 %	Ì
•				•			26.8	52.8 %
							2.4	
							6.2	
							22.9	
							4.5	
							5.4	
	· ·	· · ·	· · · · ·	· · · · · ·	· · · · · · · ·	· · · · · · · · · · · ·		22.9

#### TABLE 6. STYRENE AND COPOLYMER REEN SALES (UNITED STATES, 1963) (Total == 1.365 million pounds. including 115 million pounds re-processed)

	Appli	cati	P4		 	 		Per cent
Moulding								48.5
Moulding								13.0 61.5
Textile and paper tr								
Emulsion paint								3.7
All other uses (inclu								
Export				•				8.7
								100.0

consume 6 per cent of styrene monomer production, leaving eighteen per cent for alkyd and polyester formulations, for exports, and for miscellaneous uses.

The present paper is concerned only with styrenebased resins, as distinct from elastomers. It is, therefore, in order that we take a closer look at the markets for these styrene resins (table 6).

Biggest end-use is in moulded and extruded products of all types. Together, these two uses accounted for 61.5 per cent of total United States resin sales in 1963, but actually this sub-total is closer to 70 per cent, for the re-processed material used in moulding has here been included under "All other uses". Textile and paper treating in the present instance means mainly coating and finishing by styrene-containing latexes. Such latexes are also the basis for styrene consumption in emulsion paints which consume 3.7 per cent of styrene resins. The broad category of "All other uses" includes not only re-processed material but also styrene film and the fastgrowing category of styrene foams which will be discussed later in some more detail.

The very large group of styrene homopolymers -- mostly in the form of moulded, extruded and foamed products - pervades the whole kaleidoscope of our civilization. Table 7 shows the end-use pattern as it pertained in the United States during the year 1963.

TABLE 7.
END-USE PATTERN FOR STYRENE HOMOPOLYMERS (UNITED STATES, 1963)
(Rubber-modified types are included)

. . . . .

.

Packaging . . . . . . . . . . . .

MARCOS . . . . . . . .

-

8, 670

Mincellaneous (incl. reprocessed) . . . .

How

Refrigeration.

ing and si

Maior and small an

Radio and TV

Combs, brush

Toys, premiums, luggage, sports goods

Biggest use is seen to be in packaging, and this is followed by the many odds and ends covered in the categories of toys, premiums, housewares, and so on. Cold insulation. refrigerator trays and other uses in refrigeration equipment consume seven per cent of the total, and radio and TV, together, account for 4.1 per cent of demand for polystyrene resins.

In the main, these homopolymers are in three commercial categories: general-purpose polystyrene, and two main grades of rubber-modified impact types which differ principally in their degree of heat resistance (table 8).

Within each of these categories, there are numerous grades. The flow properties of general-purpose polystyrene can be controlled by the addition of a lubricant or plasticizer such as butyl Cellosolve stearate. These lubricants are added principally to improve the case of moulding and to aid mould release, but their introduction causes an increase in the shrinkage and a lowering of the heat distortion temperature. Choice among polystyrene types, therefore, usually depends on determining the best combination of heat distortion temperature and moulding or extrusion properties.

In general, also, resins whose mean molecular weight is relatively high are the most difficult to mould since they require very long moulding cycles. On the other hand, polymers having a low molecular weight are easy to mould but result in products which have less desirable mechanical properties. The average molecular weight of today's major grades of polystyrene calculates to 150,000 to 300,000. Historically, the long-term trend in molecular weight has been downward in accordance with the need for greater ease and speed in fabrication.

A main shortcoming of general-purpose polystyrene is its insufficient resistance to impact and its tendency to form jagged edges when it is fractured. These problems are greatly reduced in high-impact formulations. The improvement is brought about by incorporating rubber ---usually SBR - into the polymer. Originally, this was done by mechanical blending, but the bulk of today's impact polystyrenes is made by graft-polymerizing styrene on to a rubber base. This approach permits use of smaller amounts of rubber and the product has better thermal stability, processing behaviour and elongation characteristics than could be achieved in mechanical polystyrene-rubber blends.

General purpose	Soft flow
	Regular flow
	<b>Heat resistant</b>
Impact	Medium
•	High
	Extra-high
_	
Heat Resistant Impact	Medium impact
	High impact
	Extra-high impact

TABLE 0. KANNE OF FOUTSTERMENS PROTEKT	TABLE	8.	RANCE	OF	POLYTTYREM	PROPERTIE
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100.0	
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Quite naturally, impact polystyrene lacks the transparency of the general-purpose product; at best it is translucent. Its colouring possibilities are, therefore, limited to opaque products.

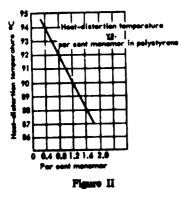
For applications in which the product is exposed to temperatures above 82°C — sometimes as high as 96°C it is necessary to select one of the heat-resistant grades of polystyrene. There are several ways in which the heat resistance can be improved. One is copolymerization with acrylonitrile or with alpha methyl styrene. Another method looks to reduction of residual styrene monomer in the product since monomer acts as a plasticizer and an objectionable one atthat, which can cause discolouration and crazing of the polymer.

The effect of residual monomer content on heat distortion temperature is brought out clearly in figure II. It is seen that reduction in monomer content from 1.6 to 0.3 per cent results in a 7°C increase in heat distortion temperature.

The problems of completing the degree of polymerization and of controlling both the average molecular weight and the molecular weight distribution are basic in the technology of manufacturing polystyrene. As in other polymerizations, the control is exercised by choice of reactor initiator and of operating temperature. However, unlike practice in GR-S rubber production, for example, styrene polymerization does not normally call for use of chain-terminating agents. The monomer itself is capable of terminating the chain at a controllable average length.

In the manufacture of pimost all polystyrene, the initiator is of the type which generates free radicals. This includes, above all, organic peroxides and hydroperoxides, used sometimes in conjunction with perbenzoator. These initiators are present in only very low concentration — of the order of one to two pounds per thousand pounds styrene. Product contamination from this source is, therefore, negligible.

As the amount of initiator is increased, reaction rate increases and average molecular weight of the polymer drops. Raising the temperature has the same qualitative effect. But it is significant that both the reaction rate and the product's molecular weight can be increased if the temperature is raised without changing the concentration of free radicals released by the initiator into the batch. Such control over free radical concentration can be



achieved by proper choice of the catalyst mix. For example, polymerization catalysts consisting of properly selected mixtures of peroxy compounds can be made to act as "trigger" systems in which a small amount of a strongly active peroxide sets off a slow peroxide. The effect can be two-fold: an increase in permissible operating temperature, and reduction in the residual monomer content.

1

In mechanics of execution, the polymerization of styrene monomer may take any of four approaches. In increasing order of their commercial utility, they are: solution, emulsion, mass and suspension polymerization.

The first technique, solution polymerization, effects the reaction in a solvent in which the monomer, and sometimes the polymer, is soluble. The product is separated from solvent, by centrifuging where indicated, and always by a vacuum drying stage. Although the method is used commercially most operators have shied away from it. There are several reasons for this: the solvent is difficult to remove from the product: highly viscous polymer solutions must be handled, and the presence of solvent in the system tends to reduce reaction rate and the molecular weight which can be attained.

The second technique is emulsion polymerization. This is of very great significance in the production of GR-S rubber. On a more limited scale, it is used for the production of high-styrene latexes of the type employed in fibreglass-reinforced moulding material and in a variety of coatings. Emulsion polymerization is also used to some extent in production of rubber-modified polystyrene. But for the production of mouldable generalpurpose polystyrene, emulsion polymerization has only limited interest.

One main reason for this is that emulsion polymerization requires use of a relatively high concentration of soap or surfactant to keep the organic phase well dispersed through the aqueous medium.

These emulsifying agents are difficult to remove from the finished polymer. The technique, therefore, results in a contaminated product which cannot be used for making colourless products. To be sure, there are some emulsifying agents available which are compatible with the polymer and, therefore, need not be removed from the product, but these materials usually tend to retard the polymerization process or result in the formation of a discoloured product.

Finally, the molecular weight obtained in emulsion polymerization tends to be too high to permit rapid moulding, though this problem could be overcome if there were sufficient incentive. The reason this incentive is lacking is that the mass and suspension polymerization processes have been developed to a high degree of commercial satisfaction.

Historically, mass polymerization is the older of these two methods. The technique involves polymerization of the pure monomer, modified only by the presence of a reaction initiator or catalyst.

There are several methods of execution. All consist of a low-temperature pre-polymerization stage to 30-50 per cent conversion and a high-temperature finishing opera-

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tion. Both batch and continuous operating methods of polymerization are employed.

The method is capable of yielding polystyrene of outstanding purity. But, one can immediately see some major difficulties which are inherent in mass polymerization processes. For one thing, it is necessary to handle highly viscous masses during the advanced stages of polymerization. For another, there is a severe problem in removing the heat of polymerization. The only way in which it can be removed from the very viscous reaction medium is through the walls of the reactor and this means that a high surface/volume ratio is required in the equipment. It also means that the batch cannot be uniformly polymerized. Unless the reaction phase is in very thin layers, the product will show a wide distribution in molecular weight composition, and it may be high in monomer content which must be removed in a vacuum stripping operation.

It can be readily seen that these inherent problems make it necessary to use fairly complex reaction equipment in mass polymerization. On the other hand, the method avoids the need to separate product polymer from an aqueous or solvent phase by centrifuging and drying. These after-processing steps are required in all of the other commercial processes employed for the production of mouldable polystyrene.

The problem of heat removal and temperature control, which causes such difficulties in mass polymerization, is almost completely absent in the suspension or bead polymerization process which operates with a suspension of small styrene globules in water. As the reaction progresses, the styrene droplets eventually harden into polymer beads which are mostly in the 40-60 mesh size range. It can be seen that such small beads provide a very high surface/volume ratio for each pound of styrene polymerized. This permits ready transfer of the heat of polymerization into the aqueous phase which is, in turn, cooled at the reactor walls.

The reaction is carried out in agitated kettles on a batch basis. In addition to water and styrene, each batch contains styrene-soluble peroxide catalyst of the type previously described. Furthermore, it is necessary to add suspension stabilizers which will maintain the desired drop-like dispersion of the organic material through the aqueous phase.

In a number of processes, these suspension agents are calcium phosphates in very low concentrations. They may be added as such or formed *in situ*. The effectiveness of these suspension agents is extended by a small quantity of anionic detergent. Concentration of both components is low enough to avoid a real contamination problem in the polymer. These suspension agents are employed in concentration ranges which have been carefully established to minimize the occurrence of bead agglomerations or mass precipitations, phenomena which result in lost polymerization batches as well as in the substantial reactor downtime.

Like mass polymerization, the suspension process is carried out at two or three successively increased temperature levels. Typically, the first 60 per cent or so of the polymerization is carried out at 90°C, a temperature

chosen low enough to avoid run-away reactions. The polymerization is then allowed to proceed to completion at 115°C. The product is centrifuged and washed with dilute acid and with water and is finally dried.

The rapid direct heat transfer from water to small globules of organic phase is the greatest single asset of the bead polymerization process. Other assets include simplicity of reactor equipment, a smaller spread in the product's molecular weight, and absence of the highly viscous materials which must be moved in mass polymerization.

Just in passing, mention should be made of a recently developed technique for polymerizing in inverse suspension, in which droplets of water are dispersed through a continuous styrcne phase and later through the finished polymer. This approach yields a product of cloudy appearance which can be cut and nailed, and has a variety of other interesting properties for speciality applications.

The general techniques employed in the production of general-purpose polystyrene resin serve also in making the major classes of modified polystyrenes. As previously discussed, high-impact polymers may be made either by mechanical blending of polystyrene with rubber or, preferably, by graft polymerization of styrene on SBR rubber. In the latter approach, styrene is polymerized by any of the four methods mentioned above, but in the presence of small particles of GR-S rubber which are suspended in the reaction batch. The product is a combination of homopolymer of styrene and graft polymer of styrene on the styrene-butadiene rubber base.

Lightweight, rigid polystyrene foams are a fastgrowing business, despite major competitive inroads by rigid polyurethane foams. In the United States, output of polystyrene foams was some 90 million pounds in 1963, and it is expected to reach 160 million pounds by 1968. Perhaps 40 per cent of total production goes into insulation board, mainly for construction applications. Other important uses include foam for packaging purposes and such buoyancy products as swimming rafts and floating docks.

Not quite one-third of all polystyrene foam is produced directly as foam board. The usual technique is to mix a raising agent, such as methyl chloride, into polystyrene powder and to mould the mixture in gas-tight forms at the plastic's softening temperature. After cooling, the material is eventually reheated to moulding temperature, and is extruded into moulds in which the polystyrene can expand under pressure from the contained raising agent.

This method has limitations in the size and type of article which can be produced. These difficulties have given rapid rise to the use of expandable polystyrene beads which now supply about two-thirds of the polystyrene foam market. Expandable beads are produced by suspension polymerization along the lines previously discussed. However, in this instance, the batch also contains, say 6-8 per cent of a light-boiling liquid, such as petroleum ether, which will not dissolve the polystyrene but is dispersed in it. To avoid premature foaming, the entire bead polymerization is carried out below SO-C. After the beads have been separated and washed, they are re-suspended and heated to 90%. whereby an increase in volume of about 300 per cent takes place. Upon eventual moulding at 110-120°C, the furning process is completed; i.e., the expanding vapour of petroleum other foams the polystyrene mass sufficiently to fill the entire mould.

In terms of present volume, the most important copolymers of styrens are, of course, these of butadiens. The big item here are the GR-S rubbers which contain styrene and butadiene in a ratio of 1.3. Copolymers of these two materials which contain predominantly styrene are used, mainly in latex form, in surface coatings and in finishing operations of the textile and paper industries. The basic techniques employed in their manufacture resemble the emulsion processes of the GR-S rubber industry.

Among mouldable styrene copolymers other than polyesters, principal importance attaches to acrylonitrilebutadiene-styrene terpolymers and to the styrene-aerylonitrile (SAN) resin formulations. In addition, there is commercial production of styrene copolymers with alpha-methyl styrene and with methacrylates. Other styrene copolymers are today strictly of a specialty character.

United States production of mouldable thermoplastic styrene copolymors in 1963 has been estimated at about 135 million pounds. Of this, the ABS resins have been pegged at 160 million pounds, and production of SAN resins at 25 million pounds.

Because of the special present importance and market potential of ABS resine, these torpolymors will be the subject of a separate paper at this meeting. For the present purposes, attention will therefore be lemited to styreneacrylonitrile or SAN resine.

This group of copolymers has been developed primarily to overcome, at relatively low economic merides, limitations in the chemical resistance of styrens homopolymers. To a certain entent, this problem can be dealt with by stress-relieving or annealing general-purpose polystyrenes. But where resistance to asids, and especially to strong aside is needed, recort must be had to appolymers of styrens. On a cost-basis, SAN regins are the most attractive answer to this problem. At a 6-7 conte-per-pound premium, these materials combine good chemical resistance with the good mouldability and unlimited colouring possibilities of general-purpose polystyrene. Also, SAN regins offer some advan age is tonsile and flosural strengths and in heat distortion temperature.

Typically, the SAN resins contain 25-30 weight per cent arrylonitrile, with the balance made up by styrone. Mean polymerination, either of the pure monomor minure or with the addition of 15-30 per cent of a modifier rash as tokene or othyl bonzone, is the preferred technology. In any event, the reaction is carried out non-setalytically between 110 and 150°C - generally near the upper end of this range. The polymerination is allowed to preceed to only about 40-60 per cent of completion. At this point, the process mix is vacuum-stripered and the volatiles are re-sirculated.

With a view to the future, polystyreus technology romans today is a highly active state of development. Improvements are being made in the basic polymoriastican technology and in the production of new and useful interpolymers with styreus. An interesting resout development looks toward the direct polymoriastical of styreus in othyl bencene in order to avoid the eastly separation of the se two compounds of which we have had accession to speak earlier.

Still other developments aim toward controlled gemetrical alignment within the polyetyrene molecule. For ecomple, instantic polyetyrene may be produced by use of Alfa catalysts or with a Zingtertype system. Such instantic polymers can be converted to highly oryanilian structures which are less brittle, more rigid and of better dimensional stability than conventional polyetyrenes. Belated technology also looks toward the development of crystallian instantic polyetyrene fibres.

These are the types of new product which may be expreted to accelerate the demand for styrene rates in the future. In the meanwhile, we may look forward to continued rapid expanden in markets for established polyatyrene types, both in the developing and in the industrially advanced actions of the world.

# 5. ACRYLONITRILE-BUTADIENE-STYRENE COPOLYMERS

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#### I INTRODUCTION

Acrylonstrile-butadiene-styrons coprilymors (ABS polymore) are thermoplastic polymors produced by either blanding styrone-acrylonstrile resins with butadionebased electomers or by grafting styrone and acrylonitrile (into polybutadione. Although sometimes classified as a special kind of high-impact polyetyrone, acrylonstrilebutadione-styrone expelymors are generally considered as a class by thempelvies. They exhibit an extraordinarily desiret le combination of mechanical, thermal, chemical, and electrical properties as well as one of processing and a medicate price.

During recent years ABS polymors have been constantly expanding into new markets as their properties are improved and their prices are reduced. While in 1968 only 40 million pounds were cold at a price of about 51 conte/pound, the forwart for 1965 is 90 million pounds, and 1963 prices range from 34.0 conte/pound to slightly over 50 conte/pound. (1) As engineering plastics they can be elecutified with sylon reseas, polyformaldeleyde acetal resize and polyearbonates. They are used where high performance with a relatively low cost is desired. Typical outlets are telephones, pipes, household appliances, automobile parts, luggage, they heels, and peologong.

#### H. MAYUPAC TURB

While the exact procedure that manufacturers us is not known at the present time, enough information is available in the literature to give a general poters of how ABS polymers can be and have been made. Two general procedures are possible, ( $\sigma$ ) mechanical blending other by mining the dry ingravitents or by mining the later of a batadione-based rubber and a styresacrylamitrile ratio (the products of which are constitute referred to as ABS type A) or ( $\theta$ ) by polymortaing styresacrylamitrile minimums in the presence of polybuladions lates (ABS uppe B). (2)

Presedures of machanish bloading are described in the early patients and over probably used to make the earlier compositions, each a Republic which was originally introduced in 1966 by U.S. Robber Co. in the form of duct each. (3) The first of these patients (4) describes a temph metadling composition prepared by bloading buildings-corplanately robber with corple-attach-dynamrams, i.e., the redder lard a high corple-attach-dynamrams, i.e., White this graduet had good preparity

compared to other materials available at that time it had various shortcomings such as lack of homogeneity, peer appearance, peer working properties and lack of a combination of a high modulus and impuet strength at low temperature. To improve these properties, various changes were made in the process the most successful of which consisted of grafting the resin onto the rubber. Other improvements were the substitution of the highacrylonitrile rubber originally used, or a portion thereof, with other rubbers, such as nitrile rubber low in aerylonitrile, (5, 6, 7) or polybutachene, (8) natural rubber. (9) styreme-butachene rubber, (10) aerylic elastomers (7, 9, 11) and/or by increasing the gel content of the rubber (6)

The more recent patents in the ABS field describe presodures in which an acrylomitrile-styrene manuare. unually 70/30, is gratical casto is rubbar, unually polybutadions, (12, 13, 14, 19) though other elastomers (16, 17, 18, 19) or mentures anylonitrile-styrene later and polybutadione intex (30) have also been employed. The polymorization is usually carried out in emulsion (12, 13, 14, 15, 16, 18, 20, 21) and the soup content is ormoal (14). However grafting of an acrylomitrile-styrens menture onto netrile rubber by a suspension polymoriastion technique has also been described (17) Still more complicated compositions are presible such as ternary blonds containing a rosin (a copelymor of styrone or a mothylatyrone with servicentirile or methacrytoentrile), a rubber (polybutadione or butadione applymer), and a graft experiment of the above meanments (21)

A typical procedure was described by Childers and Fisk in a potent result to U.S. Rabber Co. (14) in this procedure 73 parts styrence and 42 parts sorylemetrile were grafted onto 58 parts of polybuiations as a laten containing 3 parts onep, 1.7 parts moreaptan, and 0.4 part potenerus percentrations at SPC. The laten was congelated and the product was then milled for ten remutes at 320-F. The resulting polymer had a high respect drongth (fand) over at low temperatures (11.5 ft-ft)/indh metals at 25°C, 7.9 ft-ftb./imsh metals at .40°C). It desaid he used that these reported high-impact preparities are superior to these of commercially available enterhigh-impact and her-temperature-impact ABB products (an table 1). However other preparities reported in the patient (e.g., tenalls strongth, feature) modulus, and herefuers) are lower than these of commercial ABB products.

The presedure of Children and Fish seems to be of considerative eignificances class Calvert in a patent issued to Bang Warner Conposation (15) describing a similar procedure (a)pha methyletyrene was used meteod of styrene) also ones a copendang application for grafting a styrons-acrylonitrile mixture onto polybuindione A similar procedure was also described by Freemon and Stoops in a British patent (12. 24) The recent emphases in the patent literature on grafting procedures indicates that those are probably superior to mechanical blonding. This however is not necessarily true for all applications as Devenport (2) has pointed out that non-grafted, we called "ABS type A" blends have superior stiffness pr perties

A number of process conditions may be varied independently. Some of these are (a) the nature and composition of the rubber, such as type of monomor used, the temperature at which polymerization is carried out. the intrinsic viscosity and gel content, the compatibility with the roots to be minod, etc. (b) the noture and composition of the room such as styrone-acrylomitrile rate. presence of other components such as alpha-methylstyrone, motheorylonitrile, or vinyl chloride, (c) the rubber-resin ratio. (d) the use of other grafting, mechanical blanding or blanding a rubber, a room, and a graft copolymer. (a) the scap content during graft polymeriustion, (f) the extent of milling of either the functed product ed product and/or of the rubber used in making the blond. By varying these process variables it is often possible to enhance cortain properties in a composition designed to meet nations, this is done often at the engenes cortain appli of other properties. As a result, various types of ABS materials have been sailor-made for certain applications Tables 1 and 2 list a number of typical formulations with approxisibly varying properties.

# MI. PROPERTIES OF ADD POLYMERS

ABS polymors posses an encellent combination of mochanical, thormal, and electrical properties as well as chemical resistance. They are non-tonic and available in a great variety of spague science. Further advantages are superially on grafted compositions.

once of processing and term cost, and the possibility of designing grades meeting the requirements of particular applications. To illustrate this point a few examples will he estad

The impact strongth may be raised by increasing the rubber content in the resen. This is, however, accompanied by a slight reduction in host resistance, rigidity electrical proportion, and some of the other strongth proportion. If one cannot tolorate the decrease in host distortion tomporature it is possible to substitute siphs-methylstyrone for styrone (15) This of course increases the onst of the meterial

Semptimes a new idea eliminates the necessity of impairing one property in order to improve another. For most mechanical blands mailing of the rubber is necessary in order to increase its got contest. Nowever, such milling is costly and causes discustouration of the product. In order to reduce the amount of necessary milling, it has been proposed to incorporate crosslinking groups into the rubber (30) Another potent, (20) dealing with the presibility of reducing the time of the milling accessry for actuoring suitable properties describes composition propared by grafting styreme-servienstrike manufares onto a manual of polybutediame lates and a latest of servicnitrile-styrene copalymer. The products so obtained are classical to be easier to process that these obtained by grafting styrens and aprylonitrile onto polybuindions iteeff

A number of generalizations may be made. Increasing the rabber content increases the impact scrength at the seat of other properties. The use of polybuand ione rether them a butadions sepadymear gives better impact resistance at low temperature but can be used only in grafted comesitions, otherwise more than one rubber has to be used. The heat distortion samporature and other properties onn be improved by using alpha-methyletyrone instead of atyrone. A certain degree of incompatibility between the rubber used and the reason appears to be messenary,

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TAME 1. PROPERTIES OF VARIANCE ADD 10000

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Theoretical discussions as to how rubber increases the impact constance of rigid polymers have been published (2.31-32) but deal mostly with high-impact polystyrene Apparently, the rubber has to be present in discrete particles of approciable size and to have good adhosion to the polystyrene phase. Whether the runber has to be present in discrete particles in ABS polymers has not heen established (2) Some evidence against this ( vpothesis is suggested by the fact that ABS polymers are , roduced by grafting in emulsion, a process which cannot vield discrete rubber particles of approciable size, whereas high-impact polystyrene is produced in bulk or head polymerization However ABS produced by grafting gives a milky suspension of an undissolved gel, when dissolved. The presence of this got in ABS polymors may pluy the same role as the discrete particles in polyvi vrone

As mentioned earlier it is possible to improve one property at the expense of others. Consequently various grades are available and the engineer desiring excellence in one particular property for an application in which high performance in other properties is not ortical may choose the particular variety most suited to his needs Some of the grades available are (a) impact grades (high-impast, extra-high-impact, and low-tomporatureimpact) these, especially the low temperature impact. have encoptionally high impact strength, but this is solveved at the east of the tensile strength and modulus, and of thermal stability and hardness, (b) heat-resistant grades these exhibit a high heat distortion temperature but the impact strength, especially at low temperature, is lower, and the tousile properties are superior to other grades, (c) manimum flow grade (e.g. Cyoulac grade T) is especially suited for injection moulding of articles with intrionte dougne, but it has lower impact strength, (d) low-price medium-impact grades are available with good tonaile properties but they are lower in impact strength and in heat distortion temperature, (c) grades with especially good resistance to fon-fatigue (such as (voolae (38) alao posses good impact properties.

Numerous other grades are available and the measufacturers' literature should be emayled for further details.

The physical properties of the end-products are not only dependent on the material used but also on proa sting conditions. For example, moulding at a high temperature improves the gloss and heat resistance of the product, whereas the highest impact resistance and strength are obtained by moulding at a low temperature. A brief enumeration of the most important properties of ABB polymers follows

Impart strength at 73°F varies from 9 R.-Ib./iash actsh for entro-high and low-temperature-impact grades, to 15 for medium-impact grades at -40°F it varies from 3.5 R.-Ib./iash noteh for low-temperature-impact grades to 0.4 for medium impact. (22, 23)

Penalle proportion very from a tonaile strength of 0.000 pst. for modium impact grades with a tonaile modulus 400,000 (23) to as low a tonaile stor.7th as 2,400 pst., reported for comi-families cotraded-p. alloringe entrusion grade (Cycelus SP), and a tonaile modulus of 210,000 reported for ABE pige scale type B. (25) Rockwell hardness varies from R118, for modiumimpact grade  $(2^3)$ , to R62 for low-temperature grade material (22)

Heat distortion temperature varies from 230 and 240°F at 264 psi and 66 psi respectively for heat-resistant grades (22) to as low as 185 and 202°F for 264 psi and 66 psi respectively reported for Cycolac SF (25) A material verviceable at 260°F is reported to be under development (26)

Electrical properties are good but the flammability of ABS polymers procludes their use as primary insulators. This is an area where improvement is needed (22) Blonds of polyvinyl chloride ind "Blendex" ABS reinforcing modifiers are self-extinguishing.

Weatherability tests show that ABS polymers suffer some discolouration and surface degradation upon outgoor exposure. The cracks which form as a result thereof reduce the impact strength (22).

Toxicity ABS polymers are essentially non-toxic ABS polymers are resistant to aqueous acids, alkalies, salts, as well as to alcohols and to animal vegetable, and mineral oils. They are swollen by glacial acetic acid, carbon tetrachloride and aromatic hydrocarbons, and attacked by concentrated sulfuric and nitric acids. They are soluble in esters, ketones, and ethylene dichloride.

Additional details concerning the most important properties of ABS polymers are listed in table 2 and references 22 and 23

#### IV PROCINIENG

ABS polymors are available as moulding powders, pollets, and extruded sheet. The moulding composition on be pigmented or fluxed on the mill or in a Banbury minor Curing ingrediunts are not necessary as the material is thermoplastic, and sorap can be reused.

The fabrication of and products from ABS plastics is easy as these plastics can be injection moulded, extruded to shoots and pipes, vacuum formed, calendered, machined. embersed, lacquered, enumetted, printed, metallised and hundred to metal and wood ... "ast films or coatings can be obtained by spraying or brushing from setvents such as disastone alsohol. A feature important for their application as pipe is the ability to be "solvent welded This is done by pretreating the surface to be joined with other mothyl become or, proforably, with a 25 per cont solution of ABS polymor in othyl mothyl hotone Joints bonded in this manner are reported to be equal in tonaile strength to the material stack (28) Surfaces of high gloss can be obtained by "solvent polishing ich involves simple dipping in ethyl methyl hotone. (27) In addition to the various ABS materials usable per se, ABS reinforcing modifiors (brade named Blandes,) may be used with polyvinyl chileride reases. End products from Blondon-polyvinyl chloride formulations can be made to be self-entinguishing and they offer good performance efficiency (30) The dependence of propert on moulding factors has been mentioned in the provious seeties.

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## V. USES AND BCONOMIC ASPECTS

The consumption of ABS plastics was about 70 million pounds (Mlb) in 1962. (33, 34, 35) The size of the market is constantly increasing and while as recently as 1958 it was only 20 Mlb, (35) predictions for 1963 are 90 Mlb,(36) for 1965 120 Mlb (35) and 195 Mlb, (36) and the estimates for 1970 run as high as 300-500 Mlb. (34)

The exports in 1962 from the United States were 10 Mlb and predictions for 1963 are 15 Mlb. However this market may not grow since future European needs will be supplied by local production. (35)

The major markets are in automobiles, especially for instrument clusters, with a consumption of 3 Mlb in 1959, 10 Mlb in 1962, 15.8 Mlb in 1963 and 35 Mlb in 1956. (37) Telephones consumed 7 Mlb, (35) pipe 10 Mlb, (35) appliances 10 Mlb, (35) and luggage 4 Mlb. (35)

The biggest markets three years ago were telephones and pipe (17 Mlb); (35) but recently the markets for automobile parts, shoe heels, and appliances (combined sales 35 Mlb) have been growing faster. (35) Big upward surges in consumption are also predicted for luggage and pipe. (33) The approval of ABS pipes for drainage and vents in residential housing by the Federal Housing Administration (1, 35) and the potential availability of grades serviceable at 260°F should increase the market for pipes to carry hot water and steam and for certain automobile parts. (26, 35) ABS resins are well suited for use in refrigerator doors and liners because of their resistance to the fluorocarbons used to blow rigid polyurethane foam used as installation. (38) A relatively new development is the use of special ABS materials, trade-named "Blendex", as reinforcing agents to modify polyvinyl chloride.

Other uses for ABS materials include golf club heads, moulded heimets, carrying cases, moulded cams, gears, furniture, school seats, door knobs, floats, valve parts, machine housings, small machine parts, bobbins, spools, grills. household containers, sporting goods, toys, boat hulls, pulleys, packaging materials, kitchen appliances, radio and telephone cabinets, business machines, and many others.

The price of ABS plastics are constantly dropping and the number of companies entering the field is conscantly increasing. While as recently as 1960 the price range was 50-60 cents/lb. (22) 1963 prices range from 32 cents/lb. to slightly over 50 cents/lb. (1) Until recently only two companies, U.S. Rubber's Naugatuck Division (Royalite, Kralastic) and Borg-Warner's Marbon Chemical Division (Cycolac, Cycovin) were the sole producers. Two other companies, B. F. Goodrich (Abson) and Monsanto (Lustran) have now entered the field, and Marbon is marketing two additional types tradenamed Cycolon and Blendex. Other companies are also showing interest. Union Carbide has been field testing ABS materials for some time and Foster-Grant and Dow Chemical are producing ABS in pilot plants. (1, 35) The Canada Polymer Corporation also plans on ABS plant for 1964 (44) and interest has been expressed by others.

The most important competitors for ABS plastics are the acetal nylon and polycarbonate resins which are superior to ABS in some properties, but are also higher in price, (22) and high-impact polystyrene which costs less than ABS polymers but has inferior properties. A comparison of properties must, however, specify the conditions used. For example when comparing the heat resistance of nylon and ABS, nylon is far superior at low stresses; but at high loads ABS shows greater rigidity under heat. A comparison of properties and prices of some ABS plastics with some competitive materials is given in table II. Extensive tabulations and discussions concerning ABS materials as compared among themselves and with competitive materials may be found in the articles by Riley and Young (22, 23, 40, 45), particularly in references 22 and 23.

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# 6. REFINING AND PETROCHEMICALS PRODUCTION BY THE COSDEN OIL AND CHEMICAL COMPANY

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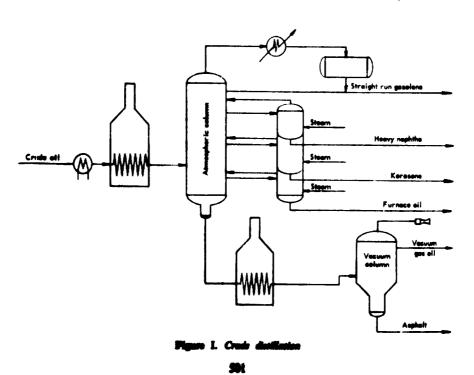
In 1952, Cosden Petroleum Corporation (now Cosden Oil and Chemical Company) brought on stream at its Big Spring, Texas refinery one of the first Udex extraction units to be built anywhere in the world. With the start up of this unit came the initiation of a long line of firsts which have conclusively established the feasibility of producing petrochemicals from raw materials generated by a 40,000 BPD refining operation. Cosden's decision to enter the chemical business twelve years ago was based on the incentive to increase product realization by converting low priced fuel products to chemicals.

At the time construction of the catalytic reformeraromatics extraction unit<sup>1</sup> was started, the Cosden refinery consisted of only five major process units. Two small crude distillation units, a fluid catalytic cracking unit, a Dubbs thermal cracker and a catalytic polymerization unit were employed to produce motor gasolene, kerosene, fuel oil, and asphalt. Since the plant was located very

<sup>1</sup> Costen uses Platformer and Udex processes under licence from Universal Oil products Company.

close to a large supply of crude oil, it was possible to produce fuel products at a very low cost. However, the Cosden refinery has an inland location which is approximately 300 miles from a major population centre. This geographical factor severely limited the profitable marketing area for fuel products due to high transportation costs. Faced with this problem, Cosden management turned to petrochemicals as a possible way to attain company growth.

Time has proven this to be a wise decision. The Cosden refinery-petrochemical plant now consists of fourteen major process units which produce eight high-purity chemicals and two polymer product lines, as well as a full range of fuel products. The flow sheet extends from crude oil to polystyrene. Although changes have been made in the refining section, an HF alkylation unit has been the only new process added for tuels production. The eight other units are all associated with petrochemicals manufacture even though the chemical complex is closely integrated with the refining operation. This paper will review the development of the Cosden petro-



chemical operation based on streams recovered from crude oil. Economic comparisons will be presented to illustrate the potential profitability of chemicals production by the processing sequence employed. The general decline of petrochemical prices will be reflected in these economics and it will be noted that operating margins are much smaller today than they were twelve years ago. In spite of this price degradation, we believe that the basic driving force of higher product realization will prevail and that production of petrochemicals from crude oil raw materials will find increased utilization around the world.

The West Texas crude, utilized by us, from the fields adjacent to the Cosden refinery is rich in aromatics and naphthenes. This is particularly true of the gasolene cut boiling in the xylene range. The mixed xylene stream produced by catalytic reforming and subsequent extraction of the reformate contains 28 per cent ethylbenzche, the raw material for styrene monomer. Normally, less than 20 per cent ethylbenzene is found in a mixed xylene stream and thermodynamic equilibrium content is only 10 per cent.<sup>1</sup> The high naphthene and aromatic content of the West Texas crude is also found in both the benzene and toluene boiling range, but to a lesser degree.

Production of polystyrene from a crude oil raw material is a complex process. Since polystyrene was the final product added to the aromatics system, perhaps we should go back to the beginning and outline the process steps which precede the conversion of styrene monomer to polystyrene. To provide a frame of reference, figure I shows a conventional crude distillation unit. This is the

<sup>a</sup> Kirk, Raymona E. and Donald F. Othmer, "Encyclopedia of Chemical Technology", vol. 15, p. 189, Interscience Publishers, Inc., New York, N.Y., 1956. first step in the process. In this unit, crude oil is separated into the various useful fractions such as gasolene, kerosene, furnace oil, gas oil and asphalt. We shall concern ourselves here only with the gasolene fraction (ASTM distillation range: 100-390°F). This stream is charged to a hydrogen pretreatment unit for removal of sulfur compounds and is fed to a fractionation system where it is separated into four cuts. This system is presented in figure II. The purpose of this distillation train is to provide maximum flexibility in production rates of the various aromatic products. If all aromatics are to be maximized, then the system can be greatly simplified to merely remove the pentanes and lighter fraction and the bottoms fraction, leaving a 150-300°F (ASTM) heart cut as feed to the platformer.

The second step in the production of aromatics from straight run gasoline is the catalytic reforming-extraction operation. In a reformer, naphthenes are converted to aromatics over platinum catalyst at a temperature of about 900°F and a pressure of 250-300 PSIG. The reformer effluent is stabilized, as shown on figure III, with the stabilizer bottoms being subsequently fed to the extraction section. In this unit, the aromatic constituents are removed by glycol extraction. The aromatic concentrate is then fractionated to yield benzene, toluene, mixed xylenes and a heavy aromatic stream which has use as either an aromatic free raffinate stream produced in the Udex extraction step is returned to the refinery for use in either gasolene or fuel for jet aircraft.

Since the reformer-extraction combination is a logical break point, and as a matter of fact Cosden stopped at this point for several years, the economics of this operation should be reviewed. Table 1 presents a material balance based on processing a West Texas crude oil such

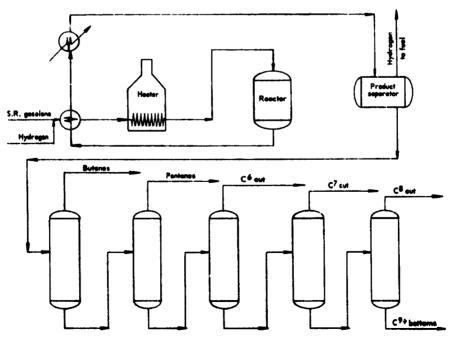


Figure II. Gausions treatment and prefractionation

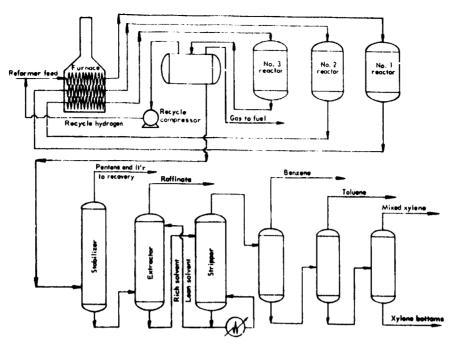


Figure III. Catalysic reforming and extraction

as that utilized by Cosden. You will note that in spite of the volume losses incurred in the reformer operation, the increase in product value is significant. Of course, the value of the straight run gasolene feed will vary from country to country as will the value of the aromatics produced. For the purpose of illustration, we have used a value of \$3.50 (U.S.) per barrel for the feedstock. Aromatic prices were set wherever possible in accordance with Oil Paint & Drug Reporter quotations on July 6, 1964. Raffinate was assumed to have the same value to the refining operation as does the straight run gasolene. The economics presented in table 1 show that product value has been increased from 1.36%/1b. to 2.15¢/1b., an increase of 58.5 per cent by the reformer-extraction combination. Operating costs amount to \$0.50 per barrel of feed (0.2¢/1b.), leaving 0.59¢/1b. to amortize process equipment and produce a profit. On a 5,000 BPD catalytic reforming and aromatics extraction combination, gross profit would be \$2,700,000 per year. Such a unit would cost about \$5,000,000 including prefractionation, product treating, and product fractionation equipment. Pre-tax return on this basis would be 1.85 years.

Unfortunately, due to the over-capacity in aromatic production units, the entire output of such a plant cannot be marketed at prices equal to OPD postings. In addition, shipping costs are incurred in transporting the aromatic products to the markets. To illustrate the combined effect of these factors on an aromatics operation table 2 presents a more realistic economic evaluation. These data reflect significantly lower prices for the benzene, toluene and mixed xylenes. The reduction is as much as 32 per cent in the case of xylenes. The effect, as would be expected, is a much lower product credit. After deduction of the 0.2¢/1b. operating cost, the gross profit amounts to only 0.2t/1b. For the 5,000 BPD unit discussed above, this would generate only about \$900,000 per year and would extend the payout period to 5.55 years before taxes. From the economics presented in table 2, it is apparent that justification of facilities to produce benzene, toluene and mixed xylenes is very difficult based on current United States prices. This is

TABLE 1. MATERIAL BALANCE AND ECONOMICS OF AROMATICS PRODUCTION Basis: OPD posted prices

-	Vol. Per cent	\$/ <i>B</i> 6/.	¢/Ð .
Feed :			
Straight run gasolene	100.0	3. <b>50</b>	1.36
Products:			
Bonzene	6.7	10.50	3.39
	16.7	8.82	2.89
Xylene	14.2	10.50	3.42
Xylene bottoms	2.4	5.88	1.89
Raffinate	40.0	3.50	1.42
Propane	1.9	1.00	0.55
Butanes	6.7	2.10	1.05
Pentance	2.5	3.36	1.55
Gas, F.O.E. •	6.9	1.25	
Loss	2.0		
TOTAL	100.0	\$5.54	2.15
TOTAL PRODUCT CREDIT		\$2.04	0.79

· Puel oil equivalent equals 6.5 M BTU/Bbl.

TABLE 2. MATERIAL BALANCE AND ECONOMICS OF AROMATICS PRODUCTION Basis: Typical refinery fob prices

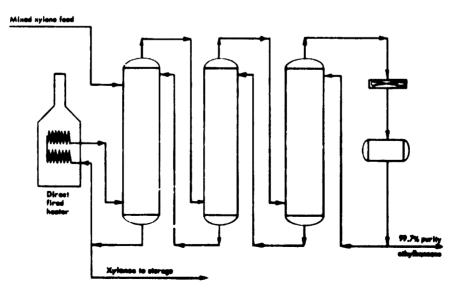
<b>.</b>	Vol. Per cent	\$/ DM.	¢)10.
Feed :			
Straight run gasolene	100.0	3. <b>50</b>	1.36
Products :			
Benzone	6.7	8.90	2.88
Toluene	16.7	6.10	2.00
Xylene	14.2	7.15	2.34
Xylene bottoms	2.4	5.88	1.89
Raffinate.	40.0	3.50	1.42
Propane	1.9	1.00	0.55
Butanes	6.7	2.10	1.05
Pentanes	2.5	3.36	1.55
Gas, F.O.E	6.9	1.25	
Loes	2.0		
TOTAL	100.0	\$4.50	1.75
TOTAL PRODUCT CREDIT		\$1.00	0.39

• Fuel oil equivalent equals 6.5 M BTU/Bbi.

not necessarily the case in other countries, particularly those either deficient in chemical production or those with a large excess of low-value straight-run gasolene. If the value of straight-run gasolene is decreased to \$2.50 per barrel ( $0.96 \neq /1b$ .), the economics shown in table 2 once again show a good return on investment. The increase of  $0.40 \neq /1b$ . in product credit reduces the payout period to 2.78 years before taxes and depreciation. This improvement, plus a potentially better aromatic selling price structure in the world market, places the reformer-extraction combination in a position for favourable consideration as a petrochemical process step.

In the middle 1950s, Cosden became aware of their unique situation with respect to the high content of ethylbenzene in the mixed xylene stream. The amount of ethylbenzene contained in this stream was sufficient to produce about 20 million pounds per year of styrene monomer. The ethylbenzene contained in mixed xylenes was worth between 2.4 and 3.6 cents per pound depending on its use, while styrene monomer was selling for 16.5 cents per pound. Once again the driving force of increased product realization led Cosden to take the second step toward polystyrene from crude oil. When the decision was made to build a superfractionator to separate ethylbenzene from mixed xylenes, it was considered impractical due to a difference of only 3.9°F between the boiling points of ethylbenzene and paraxylene. In spite of the many opinions that separation of ethylbenzene by fractionation was next to impossible, Cosden, with the assistance of The Badger Company, Inc., erected a 600-ft. column which went on stream in February, 1957. Instead of proving to be an engineering fiasco, the superfractionator performed even better than was anticipated. The process has now found world-wide acceptance and is being used by five other companies under Cosden licence. Although the first commercial unit to separate ethylbenzene from mixed xylene was employed under ideal conditions (that is, with 28 per cent ethylbenzene feed), this high concentration is not essential to successful use of the process. Commercial operating data has now substantiated the suitability of the process for recovering ethylbenzene from feeds containing as little as 15 per cent. It is also possible to utilize aromatic streams produced from naphtha cracking operations as a raw material.

Figure IV shows a flow diagram of the ethylbenzene separation section of the plant. Mixed xylene feed is introduced through any one of several feed points into the 600-ft. superfractionating column. This column is split into three 200-ft. sections which operate in series. The sections are connected by vapour lines which carry



Planes IV. Ethelbensons reservery

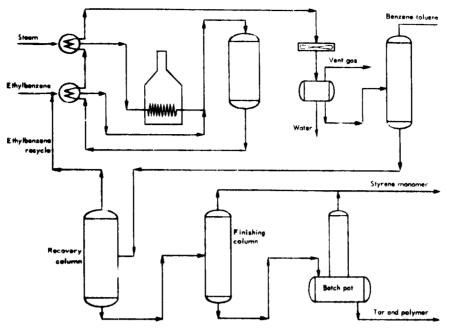


Figure V. Styrene monomer production

vapours from the top of the bottom section to the base of the middle section and from the top of the middle column to the bottom of the upper section. Intermediate reflux is pumped from the bottom of each column to the top of the next lower portion of the tall tower. Heat is supplied to the lower column by a direct-fired reboiler. The overhead vapour from the top column section is condensed by air-cooled heat exchange and collected in a conventional overhead receiver. Both the reflux and product streams are withdrawn from this vessel.

In spite of its size, the ethylbenzene fractionation column is very stable. The time delay is great due to the large holdup of liquid in the tower. Column inventory is roughly 1.5 times the daily charge rate; therefore, it sometimes takes one or two days before a change in operating conditions is fully realized. Once steady state operation is attained, this is a real advantage for the system. The product ethylbenzene is a very high purity material. To produce polymer grade styrene monomer, the ethylbenzene must be at least 99.6 per cent pure from the standpoint of xylenes. In the seven years operation at Cosden, this has never been a problem. On several occasions the ethylbenzene has approached essentially 100 per cent purity.

In conjunction with the ethylbenzene separation unit, a unit for producing styrene monomer was added at the same time. This unit, like the superfractionator, was a Costen-Badger design and included several novel features, the most significant of which was the separation of styrene monomer from unconverted ethylbenzene in a single vacuum distillation column. Heretofore, this separation had been accomplished in a two-column system operating in series. Since only about 35 per cent of the ethylbenzene is converted in one pass through the dehydrogenation reactor, the ampunt of ethylbenzene recycle

is quite large and the single-column separation represents a substantial saving in utilities cost. In comparison to the fractionating columns which yield ethylbenzene, the styrene production unit is a midget. Figure V shows a process flow diagram of this unit. Fresh ethylbenzene is pumped to the unit from storage, is combined with recycle ethylbenzene, and the mixture is preheated by heat exchange with reactor effluent. Saturated steam picks up some superheat by exchange with reactor effluent and is heated to final reaction temperature by a direct-fired superheater. The mixture of ethylbenzene and steam (2.5-3.0 pounds steam/pound of ethylbenzene) passes downflow through a bed of iron oxide catalyst. Reactor effluent is cooled by heat exchange with incoming feed and steam and is then condensed by air-cooled exchangers. Condensed liquid is collected in a surge drum where water is separated and light gases are vented.

The crude-styrene reactor product contains 35-45 per cent styrene. The balance is predominantly ethylbenzene, although 4-6 per cent benzene and toluene are present as products of side reactions which take place during the dehydrogenation step. Crude styrene liquid is first fed to a small column for removal of the benzene and toluene. Bottoms from this column are then charged to a 185-ft. tall vacuum distillation tower containing a large number of tow pressure drop trays. Ethylbenzene recycle is removed as an overhead product. Styrene monomer, essentially free of ethylbenzene, feeds continuously to a small finishing column which separates the styrene from small amounts of tars and polymers. These heavy ends are collected and further distilled in a batch-type column for further styrene recovery. The continuous finishing system employed at Cosden has proven to be very satisfactory and economical to operate. At the time the Cosden plant was built, almost all styrens producers used batch-finishing systems and many of them still do. Purified styrene monomer (99.7 to 99.8 per cent purity) leaves the finishing system and is sent to storage where it is continuously circulated through a refrigerated cooler to maintain a storage temperature of about 65°F.

Let us now examine the economics of this second link in the crude oil to polystyrene chain. As was presented earlier, the xylene stream produced by reforming and extraction has a value of 17¢/gallon, i.e. 2.34¢/lb. The increase in product value obtained by recovery of ethylbenzene and production of styrene monomer is shown in table 3. This economic study is based on processing 1,000 BPD of mixed xylenes containing 28 per cent ethylbenzene. A recovery of 90 per cent was assumed for the fractionation step resulting in the recovery of 250 BPD of 99.7 per cent ethylbenzene. A styrene monomer yield of 87.5 per cent by weight was used as the efficiency of the dehydrogenation step. Benzene and toluene production amounts to 6 per cent by weight based on ethylbenzene disappearance. Based on the yield structure presented above, the incentive for producing styrene by the ethylbenzene recovery route is indeed significant. Product value is increased by 1.33¢/1b. or about 57 per cent based on the value of the mixed xylene feedstock. The cost of operating the conjoint ethylbenzene recovery-styrene monomer facility is very low in comparison to the cost of the old-established alkylation method for ethylbenzene production. Combined operating cost amounts to only 0.49¢/lb. of feed processed, leaving a net profitability of 0.84¢/1b. or \$2.56 per barrel of xylene feed. Plant investment for a unit to recover ethylbenzene from 1,000 BPD xylene feed and to convert this ethylbenzene to styrene monomer is estimated at \$3,000,000. Profit before taxes and depreciation on the 1,000 BPD unit is \$896,000, resulting in a pretax return of 3.35 years. Once again we see the effect of depressed chemical selling prices on a small operation.

TABLE 3. MATERIAL BALANCE AND SCONOMICS OF STYRENE PRODUCTION PROM MIXED XYLENE PEED

	Jbis.	₩1. %	¢/ <b>ib</b> .
Feed :			
Mixed xylene, 28 per cent			
ethylbenzene content	1,000	100	2.34
Products :			
Styrene	209	21.9	8.60
Benzone and toluons*	15	1.5	2.00
Xylenes	750	75.0	2.34
Ges and loss	26	1.6	
Total	1,000	100.0	3.67
TOTAL PRODUCT CREDIT			1.33
Operating Cost.	<b>. .</b>		0.49
Net Profitebility			0.84

 Value set at 2.0¢/# since this stream must be represented for recovery.

This particular case is extremely sensitive to styrene monomer selling price. For example, 1.0¢/1b. increase in the styrene price reduces the payout period by 1.65 years on a pretax basis. It is not difficult at all then to visualize the incentive for Cosden to enter the styrene business on a relatively small scale when styrene monomer was selling for about 16.0¢/1b. By the time the Cosden unit came on stream, the price of styrene had dropped to 12.5¢/1b., yet the unit still showed an attractive return. Since 1957, as the price of styrene has steadily decreased, the Cosden plant has been expanded in capacity. The natural ethylbenzene supply has been supplemented with synthetic ethylbenzene produced by alkylation of captive benzene. The plant is now five times its original size and produces 100 million pounds of styrene monomer annually. In spite of all these changes, the original ethylbenzene recovery system is the heart of the operation and produces the lowest-cost ethylbenzene available.

Ethylbenzene is not the only portion of the mixed xylene stream which can be upgraded. The remaining ortho, para and metaxylene isomers can be efficiently separated into high purity compounds for use as chemical intermediates. This is done at Cosden by the use of fractionation, crystallization and a new separation technique known as clathration. Orthoxylene can be separated by conventional distillation from the bottoms stream leaving the ethylbenzene recovery tower. At Cosden, this separation is made by operating the ethylbenzene column in a "blocked-out" manner. The bottoms stream from the ethylbenzene separation is accumulated in storage and fed back through the same columns as are used to recover the ethylbenzene. The tall columns are not required for orthoxylene recovery; however, excess capacity existed in the Cosden unit making the cyclic operation very economical. Actual distillation requirements for orthoxylene are quite reasonable. A column containing about 150 trays and operated at reflux ratios in the range of around 10:1 is normally used.

With both the ethylbenzene and orthoxylene removed, the economics of paraxylene recovery are greatly enhanced. Paraxylene is separated by fractional crystallization which requires low temperature operation. By removal of the two components mentioned above, refrigeration load is significantly reduced, thereby lowering operating costs. Unfortunately, a eutectic mixture is encountered in paraxylene crystallization which precludes complete recovery of the para isomer. Recoveries of only 60-65 per cent can be obtained while producing a 99 per cent purity paraxylene product. The mother liquor from this operation is a stream containing about 75-80 per cent metaxylene with a 12-15 per cent paraxylene concentration. Working in collaboration with Union Oil Company of California, a new separation method has been perfected by Cosden for producing 95 per cent metaxylene from the 30 per cent concentrate. This process utilizes a Werner type complex and is known as clathration. A semicommercial unit was erected in 1962 to develop the clathration technique. The process is now ready for commercial application to the production of 95 per cent motaxylone; however, due to depressed world market prices for phthalic anhydride, which has a marked

effect on isophthalic acid business, no large-scale units have been built.

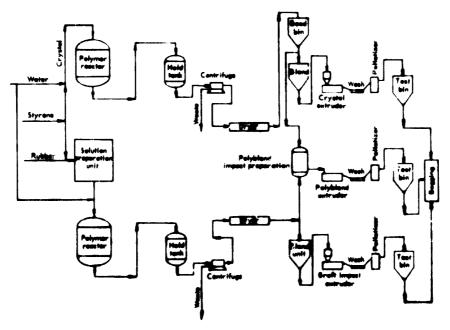
The final step in the polystyrene-from-crude-oil story is the polymer production facility. This unit came on stream in the Cosden complex during the summer of 1958. Of the several methods of polymerizing styrenesuspension, mass, emulsion and solution — the suspension system was selected chiefly because of the excellent quality control which it offers. The original product formulations and techniques used were developed by an independent consulting laboratory. In the past six years improvements and changes have been made in this original work and at this time one would scarcely recognize the Cosden process in comparison with the process of 1958. In general, suspension polymerization is a process by which a liquid monomer is converted to a fully polymerized hard bead in the presence of water and suspending agents. Catalyst and heat are used to attain the desired reaction rate. Polymerization takes place in a glass-lined agitated reactor. The size of these vessels may be 2,000 to 10,000 gallons depending on plant capacity. The number of reactors also depends on plant size. Temperature control in the reaction vessel is maintained by a hot water circulating system. This system is capable of controlling reactor temperature to within 1°F, even during the period of greatest heat liberation.

A simplified process flow diagram is presented in Figure VI. Two separate lines are shown for crystal and graft impact polymers. The reactor is first charged with process water together with the appropriate amount of suspending agents. To this mixture is added styrene monomer, catalyst and other chemicals as required by the particular formulation. The agitated mixture forms itself into a suspension of fine droplets of monomer in the continuous water phase. Reaction temperature is then increased to the desired level and maintained with agitation for 10 to 20 hours. Both the operating temperature and the exact cycle time depends on the particular product being produced. During this period of long agitation, the monomer passes through sticky, soft and finally hard bead stages. When the reaction is complete, a slurry of polystyrene beads, 40-60 mesh, is obtained. This slurry is transferred to a hold or wash tank which frees the reactor for another charge. In addition, the hold tank serves as a feed tank for the centrifuge.

The preceding discussion applies both to the crystal and graft high impact polymers. In the case of the high impact material, rubber preparation is necessary and other process steps must be added to cause the styrene and rubber to copolymerize properly. Also, as one might expect, processing conditions differ greatly for the two products.

The slurry of polystyrene beads is constantly agitated in the hold tank and is then fed on a continuous basis to a solid bowl centrifuge. Due to the gravity difference between the polystyrene beads and water, the beads move to the wall of the bowl. There, a screw conveyor built into the centrifuge moves the beads along the wall of the bowl and out of the water phase. Wash water rinses away residual chemicals and the wet beads are de-watered in the last stage of the centrifuge. The next processing step is complete removal of moisture by the use of a hot air rotary drier. The hot beads from this drier are discharged into an air conveyor which carries them to the storage bins for quality control testing.

Depending on the formulation, lubricants, stabilizers, and inhibitors need to be added to the polystyrene beads before they are processed into final form. It is also necessary to blend crystal and graft impact to produce medium impact polyblend products. Various types of mixing and



Planto VI. Aubatyrone production

blonding methods are employed in this sources of the plant. After the proper amounts of chemicals have been added to the heads in a blending step, the mixtures are fed to one of several large extruder lines. In the extrusion step the heads are blended, melted and mesticated by the extruder screw as heat and pressure build up. The product emerges as a series of small strands that are pulled through a water trough for cooling and into large pelletizing machines. There the strands are chopped into pellets of 1.16-1.8 inch in length and diameter. The pellets discharge onto a screening table for size classification and are then conveyed by sir to either finished product storage or to the bagging and loading operation.

The Condon polystyrene process is capable of producing two basic products and numerous variations of each of these. The two basic types are crystal polystyrene and styrene rubber graft high impact. Before proceeding into a short discussion of the various grades of polystyrens and their nore common uses perhaps it is well to define the terms crystal polystyrene and graft high inpact polystyrene. The term crystal polystyrene, as generally used, means a polymer consisting primarily of pure styrons homopolymer with only minor amounts of lubricants or other additives. The term graft high impact has been applied to the sopolymer of styrene with rubber because the styrene molecules graft or attach themsel on to the unancurated bonds of the rubber ohain. This sopolymoriantion improves the compatibility of the materials, hence a more translucent product results than in the case of physically blended impact materials Also, this copolymorization greatly improves the impact strength of the polymor

Although numerous crystal polystyren-s can be made. there are three types which are the most important. These three materials or ver the broad needs of industry from thin-walled food containers to thick-section items such as refrigerator trays and extruded shapes. The first type of orystal is the easy flow, fast set up type. This is a polymor designed with a low heat distortion and low molecular weight to give it the onse of flow necessary to fill multisavity moulds. Common uses for this product are medicine visis, food containers, compartmented beass and other items where high-spend moulding is needed. The second type of orystal polystyrene is the medium or standard flow material. This product is somewhat stronger than the ency flow materials and has a slightly higher heat distortion. It is primarily used in moulding small parts such as clothes pine, drinking placess and trays. The third important type of orystal is the high-heat distortion grade. This product is uses in applications where strongth and elevated use temperature are eritsed it moulds very rapidly and, due to its molecular weight, is the strongest type of crystal made. As is the case with the other two types, the product is crystal ultear and free of foreign master. This product may be entruded into shaped articles such as light diffusors and ornarisontal strips.

Several graft impact polymers may be produced, but, as was the once with crystal polystyress, there are three important types of product. These are modium impact, high impact for mrubing, and high impact for extrusion. Due to the onet of high-impact polystyress, must contain

ners and other disposable ners requiring more strongth than can be obtained with crystal are made of machum impact polystyrone. The modern impacts may have proportion anywhere between those of orvital and high impact. The material is very translucent and is especially designed for containers and other then walled objects The high impact opposibily formulated for injection moulding has good flow characteristics, high impact strength and good transhuosnee. This latter property makes it especially applicable to fend containers and hoxes where strength must be obtained without producing an opaque nom Another variation in the high-impact moulding grades is a product shibiting good remotones to shook loading. This product is designed for refrigerator isnors, high-quality toys and other long use stoms. The third major form of high impact polystyrons is a product formulated for containers and container lide produced by vacuum forming of entruded sheet. The product has the high-heat distortion necessary for lids for hot drink cups, but has the floxible characteristics required for saly processing.

As can be seen from the discussion show, this polystyrene process is a flowible one that can produce as influite number of types of orystal materials. The process has yet to fail to be capable of producing a special type of crystal polymer. Normally, a new type may be produced without experimentation provided the formulations are varied by someone with a broad knowledge of polymorization. The greft high imposit products one also be varied over a broad range Rubber content may be varied at the reactor or later by changes in the blending section of the plant. Greft production is somewhat more complicated than crystal and some experimental formulations work is usually required to perfect a new product Nevertheless, the suspansion polymerimation technique and in the Coden process allows superior quality control which is an essential key to process versuality.

Polystyrone conomics are extremely sensitive to product mix due to the wide differential between the price of orystal and high impact polymore. For the purpose of illustrating the contonios, we have selected a product mixture of \$9 per cent erystal and \$9 per cent impact Dasad on solling prices of 13.0p/1b. and 20.0p/1b. respostrooty, the everage polystyreme price is, for this example, 16.50/1b. Table 4 presents polystyrens economies for a 40 million pound per year plant. These componence Mustrate the importance of plant case for profitable polystyrone manufacture in the United States. Based on an investment of \$3,000,000 for the 40 million pound per year plant, a payout of 2.56 years before taxes and depressation results from the 2.9\$/16. not profitability As will be noted, the operating cost of 3.7\$/16. 16 56 per cent of the product credit. Even in the case of a 40.0 million pound plant, over 2.05/1b. of the operating casts are fixed and would remain constantly constant suspective of plant size. The reasons for this abaormally high ratio of fixed operating costs to variable cost is the large amount of labour required to operate and mainteen the plant. At the high labour costs, experienced in the United States, this is a major faster. In other countries of the world where the cost of indexer so issuer, say polychyreae units should be quite feasible. A reduction

In labour costs of 20 per cest would increase ast profilibility by 0.50/b in the 40.0 million pound per year care. This effect, of course, would be far over-shadowed by increased polystyrene with for almost twise the current the world polystyrene with for almost twise the current 1 hited States of America price. Styrene monomer is this more expensive but not in assify the same ratio. The price differential is, therefore significantly higher than that shown in table 4. This being the asse, very small, i.e. 18-15 million pound per year polystyrene plants could be very attractive investments in animitries that are only beginning to develop a petrochemical business.

To illustrate this point let as consider the economics of producing 10.0 million pounds per year of polystyrene at a hypothetical location. The following assumptions were made as to conditions existing in the area.

- I Styrone monomor available at 10.00/th
- 2 Other raw materials available at 10 per cent above United States prices
- 3 Labour cost at 90 per cost of Linsted States cost
- 4. Utilition onet at 300 per cent of United States price.
- 5 Perivatyrone selling price equal to 180/16 for orystal and 360/16 for impact.

The economics of this operation based on the above assumptions are shown in table 5. A comparison of these conomics to three presented in table 4 reveals several factors of significance. Due to the higher selling prison for polyntyrone gross product credul is up from 6.60/th of polynter to 12.320/th, an increase of almost 160 per cent. Operating costs expressed as cents per pound are almost ensetly twice the cost of operating the 40.0 million pound plant in spite of the lower labour cost used in the 10.0 million pound case. Had the same labour cost been

TABLE 4. POLYNYNAME BOUNDARE'S

Buris 48,600,600 pounds par yaar 90 par cont crystal polystyreas 90 par cont graft impact polystyreas

		fið. í yvitr	tið palpage
New materials			
Styrano mananer		40,000,000	8.6
Rubber		1,488,680	30.0
Lubringet.		1,000,000	10.0
Products:	Torn.		••
Crystal palpatyrese		30,000,000	13.0
Nigh immet gebeteren			204
	Terns.		M6.5
Gress grediest credit			6.6
Opuniting cash			3.7
Net profiledably			2.9

# TABLE 5 POLYNONIC BOOMONICS

	and a second second second second second second second second second second second second second second second		
	h ver	2.16	etta outvaner
Ann Materials			
Styres a menomer	F47,68889 13889	10.0	
Rubber	46-7 (MMH)	11.0	1 21
L ubraam	2.963 (1998)		0.27
Products EOFA	I		11.46
( rystal polystyreas	C		
High impact polyatyrene	5,0000,0000		
reality templater persystery raise	5,600,000	¥().()	
TOTA	L		24 (18)
Gross product credit			12 52
Operating costs Pixed			5 64
Variable			1.85
Not prolitability			5 64
Plant inventment	\$1.000,000		
Greek annual profit	194,600		
Payout	2.0 /001	*	
	. , ••••		

Before taxes and depreciation

used for the small plant, operating costs would be 10.34g; b. or almont three times the per pound cost of operating the 40.0 million pound per your plant ft is, therefore, Parther emphasized that labour costs are extremely important in the production of polystyrene in small plants. The major significance of the economics presented in table 5 is that they show a very attractive return on a small plant in an area where polystyrene prices are high and operating costs can be controlled at a low level On an investment of \$1.000,000, gross profit of \$504,000 before takes and depresention would be realized. This is a 2.0 year payout, which based on current United States conditions is a very attractive project.

Both the methods and the seenomics of producing polystyrone from grade oil have been reviewed at some longth, but little has been suid about the potential quantity of polymer which can be produced from a nerol of orude From 40,000 DPD West Texas crude, Coston produces 20 million pounds per year of aromatic products. This is 6.75 per cost by weight on orade col input. By recovery of ethylbonauts from mixed sylence using the processing scheme presented in this paper, polystyrene production would be 22.6 million pounds annually or 0.53 per cost yield from orude. This is only first stop yield structure, and not an ultimate yield. mumo can be alkylated to othylbeasone by any one of several basws pressure. With the addition of alkylation tes to the estabytic reforming, aromatics entraction, hythenness recovery, styrons monomer and polystyrone support, the yield of polymer from orade can be drasti-ily morecased. In the Condon operation, 46.7 million to per year of beamone is produced. Conversion of n material to polystyrene increases annual polymer

production to 77 million pounds. The potential polystyrems from the 40,000 BPD West Tonas crude is then 1.79 per cost after the around step is taken.

Petential arcmatics from orade vil vary widely for different types of oracle. To manimum profiles, it is important to operate the refining-petrochemical plant on the optimum oracle available. Evaluation of arounderin potential from a particular oracle is an eccential step in these economics studies. Over the years Coulom has done a large amount of inheratory evaluation work in this area. Methods and techniques have been developed which have preven to be quite reliable. In addition to being a great asset to the Coulom operation, this oracle evaluation technology has been used extensively in Heemaing othylbeasets recovery, styrens monomer and polyatyoene processes. Petential feedbacets have been acknowled by

prespective Hassesses and, based on inferencery evaluation, Conden can determine in effect the account of polyetyrese which can be preduced from that specific crude oil.

The development of the arcmathe destance complex at Conden has openned more than a destable it has been a period plagmed with problems of destancing prices with over-sequently existing for many products. Noverthehes, we have been concered on a wood products beyon the secons and have at all times condenvaried to take minimum advantage of our row material position. Perhaps this is the secon to our success. We have that the study-off-to-pelystyrese story has been helpful and that is some small way has contributed to varie is destable in some small way has contributed to would de generation of products is then which will be used to further industrial development in developing countries.

# 7. NYLON

# Professor Louis F. Nuseh, University of Tenne, USA

Nylon is a generic term for a polyamsde rean Remme of this type can be formed by condensation polymerization of a disorboxylic auid and a diamine (nylone fit and 610) and by the polymorization of an amoge amine acid (nylone 7 and 11). Nylone also can be produced by the polycondensation of lactame (nylone 6 and 12). Table 1 contains a list of various sylone which are produced commercially and those which are receiving active study as to their commercial potential (1).

The name given to a sylon is derived from the monomer or monomers used in its production. For example, sylon 66 is the product of the condensation of honomethylonodiamine, a sin-carbon diamine, and adipic sold, a sin-carbon sold. The monomers for sylon 610 are honomothylenadiamine ( $C_a$ ) and vebacic acid ( $C_{ia}$ ) The nylon numbers (e.g. Af and 610) indicate the carbon atom number of the diamine followed by the carbon atom number of the disaribonylic acid. Nylons obtained from a single monomer, either a loctam or an omega amono aoid, are named so as to indicate the carbon number of the monomer. For example, caprolactam, a wa-carbon compound, is the monomer from which nylon 6 is produced.

While the chemical structures of the two broad types of sylons are similar they are not identical. The condensation product of a diamine and a dicarboxylic acid has the following sequence of groups. Nylon 66 serves to illustrate this type of sylon.

			~
	findentrief states	(2) 2. Contradicts a public community of the state of the state and state.	
		<b>Name</b>	<b>Formula</b>
6	Communetat	Caprolastam	
-	Commercial	Adipis acid Manasatilipianadiaanina	NGOC-(CN,)-COON N,NCN,-(CN,)-CN,NG,
	Commercial	Salanis anti Haranathylanadiamine	NOBC-(CR.)-COON N-ACRACRCR.M.
H	Community (Bureps)	13-Amhoundmanete and	N_MCN_4CN_+COON
3	Beparimentan	Various p-lastans	
•	Begentimentul	3-Pyrrolidame	CN, CN, C-0
9	Begentennental	Valeralizataan	
7	Brechgingstud	7-Andreheptensis calif at	NUMERIC CONTRACTOR
	_	Bibyi Teminuhapianasia	NJICH, CH., CONCH, CH.
•	<b>Conjunction</b>	CupyHastasa	<b>CHCH_2</b> -C-0
9	Reportmental	Manimpalungania anti	HANCHARCHAR COMME
10	Engeninunt gi	Longitudian	Cit, - City, C-0

TABLE 1. TYPES OF HYDER

Nylon 6 is an example of a nylon produced from a single monomer.

	0	0	0	0
Nylon 6	C (CH <sub>2</sub> ), CH	NH C (CH)		CH,NHC(CH,),CH,NH

TABLE 2 WORLD-WIDE	DISTRIBUTION OF	NYLON	PLANTS, 19	64
--------------------	-----------------	-------	------------	----

Location	Number of planes *	Location	Number of plants
North Amorica	31	Western Europe.	
Canada	2	Bolgium .	1
Menieo	. 4	France.	4
United States.	25	Haly	
South America	23	Luxembourg Netherlands	1
Argentina		Nerwey	í
Dranil	3	Perhani	i
Chila	. Î	Spain .	ġ
Colombia	3	Swalan	2
Peru		Switzerland	3
Uraguey.	3	United Kingdom	8
Venemete	4	Fed. Rep. Germany	11
Eastern Europe	20	Middle East	4
Czecheelovakin	2	brasi	1
Bastern Germany	4	Turkey	2
Greese	1	UAR .	1
Hungary	2		•
Peized	1	Per East	2!
Romania	1	China (mainland)	3
USBR	9	india	6
instralia.	2	Japan	•
	6	Rep. of Korea	2
		Chine (Taiwas).	1
	TOTAL	156	

Including plants projected or under construction.

The difference in structure is subtle but none-the-less real. The properties of nylon 6 and nylon 66 are similar but not identical.

Only nyion 6 and nyion 66 are currently of industrial importance. Nyion 6 was developed in Germany by I. G. Farbon at eccentially the same time that du Pont was developing nyion 66 in the United States. Because of patent restrictions and raw material considerations, sylon 6 has been the nyion most extensively produced in Europe and nyion 66 is the nyion most extensively produced in the United States. In the United States the 1965 nyion 66 enganity will be cs. 300 million pounds and there will be appreximately a 300-million-pound capacity for nyion 6.

The world-wide distribution of nylon plants is given in table 2. The reason for nylon's popularity as a fibre (its most important use) is its combination of strength, toughness, and elasticity which is still unmatched even by polyester and polyacrylonitrile fibres. Nylon is so universally accepted today that the name appears in almost every known language and dialect. In some areas of the world "nylon" not only designates the fibre but also signifies snything which is superior among manmade objects or schemes.

#### PROPERTIES

The properties desired in a nylon resin are determined by the proposed use of the resin. The melting point (table 3) and the amount of water that can be absorbed by a nylon are especially important for fibre applications. Other general properties such as stability and solubility are of importance regardless of the intended use; and strength, elasticity, toughness, flexibility and abrasion resistance are other important characteristics. No single nylon excells all other nylons in desirable properties; in fact, they are all remarkably similar and the choice of nylon is usually dictated by economic considerations except for specialized uses. It is customary to use nylon 66 as a standard of comparison for the other nylons, at least in the United States.

#### Nylon 66

Nylon 66 is characterized by high strength, elasticity, toughness, and abrasion resistance. These good mechanical properties are retained up to 150°C but an upper limit of 125°C is desirable for plastics use.

Phonols, cresols and formic acid will dissolve nylon 66 at room temperature but nylon-66's solvent resistance to other compounds is good. It can be degraded by strong acide and. at elevated temperatures, by hydro-

#### TABLE 3. MELTING POPPTS OF VARIOUS HYLONS

	Vyd		 						<b></b>		hist	<b>ing point</b> . *C
	<b>i</b> .											223
												265
619	).			·			•	•	•	•		215
						•						190
-						•						265
-						•						203 200
_						•						20
						:						100
		÷		÷	÷	÷			Ż	÷		179

lysis. These properties account for the degeneration of nylon stockings, etc., when sulfur dioxide exists in the atmosphere under moist conditions. The general outdoor weathering properties of nylon 66 are only fair unless it is specially stabilized. Nylon 66 will discolour in air at about 130°C. The moisture resistance of nylon 66 is poor and its electrical uses are restricted to low frequencies because of the polar groups in the polymer.

#### Nylon 6

The properties of nylon 6 are, in general, similar to those of nylon 66 except for the lower melting point of nylon 6. It is also somewhat softer and less stiff.

#### Other nylons

Nylow 610 has a lower melting point (215°C) and lower moisture absorption than either nylon 66 or nylon 6. Because of its lower moisture absorption, nylon 610 retains its stiffness and mechanical properties better when wet than does nylon 66. The lower melting point and moisture absorption are attributed to the additional hydrocarbon character of the sebacic acid ( $C_{10}$ ) unit in the polymer. Nylon 11 is the least water sensitive of the commerical nylons because of its greater hydrocarbon character ( $C_{11}$ ). The water absorption of nylon 4 is appreciably greater than that of other lactam polymers and equals that of cotton. Such water absorption of nylon 4 would be expected because of the high "atio of polar amide groups to methylene groups.

The melting points of nylons formed by the polymerization of lactams decrease with an increase in the number of carbon atoms in the lactam (table 3). A nylon with an even number of carbon atoms in the monomer has a lower molting point than either the next higher or next lower nylon.

#### **APPLICATIONS**

Whether or not a country builds a nylon plant is intimately associated with the applications or uses of nylon (table 4) and the relationship of these uses to

TABLE 4. USA NYLON USE PATTERN, 1964	TABLE	4.	USA	NYLON	UNE	PATTERN,	1964 *
--------------------------------------	-------	----	-----	-------	-----	----------	--------

	u		 -	. ـ		_	 	Millions of pounds	) <b>Per</b>	CONV
Hamont yern								660		86
The cords .								229	29	
Apparel								130	17	
Carpets, rugs	۱.							110	14	
Industrial.								70	9	
Hostery .								45	6	
Upholetery .								35	5	
Other (+ en		Ò			÷	÷	÷	<b>9</b>	6	
aple Stee									-	
louiding rasis										6
						ħ		770		100

Prom Chemical Wook, 22 August 1964, p. 132.

TABLE 5. PREDICTED USA SYNTHETIC FIBRE PRODUCTION, 1965 .

-				bre						Millions of pounds	Per cen
Rayon .										960	41
Nylon .										700	30
Acetate										305	13
Acrylic.										210	9
Polyeste	<b>r</b> .		•							165	7
							Ť	ж	AL.	2,340	100

\* From Chemical Week, 15 December 1962, p. 38.

the needs of the country. Because of the unique properties of the nylons it is possible for them to be used both for the production of synthetic fibres (table 5) and as a moulding resin (table 6).

#### Nylon 66

Nylon 66 is well-suited for the production of fibres because of its combination of low modulus and high elasticity combined with strength and toughness. These characteristics are of special importance for general apparel use including hosiery, undergarments and dresses. Small-denier textured nylon yarn — stretch nylon accounts for nearly half of nylon's apparel use (excluding hosiery). This type of nylon is used primarily for infants' and children's wear and men's and boys' clothing. Tufted broadloom carpeting accounts for about 80 per cent of all broadloom carpets and represents one of the single largest uses of nylon 66 (table 7). "Broadloom" is a generic term covering any woven, knitted, or tufted carpet made on a loom or machine six feet wide or wider

Industrial uses of nylon 66 include rope, thread, and cord in which high tenacity and good elasticity are important. Nylon's resistance to abrasion and to chemical attack recommends its use in belting and filter cloth. Nylon filter bags are expecially suitable for cleaning gases from such sources as cement kilns, steel furnaces, non-ferrous metals operations, fertilizer dryers and carbon black plants.

The production of tire cord is the largest use of nylon 66 fibre in the United States (table 4). Nylon cord in tyres gives added safety since nylon, weight for weight, is 60 per cent stronger than rayon, runs cooler, and resists

TABLE 6. PREDICTED USA NYLON MOULDING REEN USE PATTERN, 1965\*

		·		_		ør	 			 -	Millions of pounds	Per cent
dect		-	ION	ł	i.	•					26	52
latra	der	١.				Ξ.					12	24
dena											10	20
	•										2	4
									т			100

\* From Chemical and Inglusering News, 20 May 1961, p. 80.

impact better. However, at the present time virtually all original tires on passenger automobiles have rayon cord. The main reason is flat-spotting of nylon cord tyres. Fibre companies are actively trying to correct this defect in nylon tyre cord. A recent development is the introduction by du Pont of N-44 nylon, a polyamide of *m*-xylenediamine and adipic acid. Nylon tyre cord is used as original equipment for most heavy-duty applications such as truck and airplane tyres. Nylon cord is used extensively in replacement tyres.

Nylon 66, and other nylons, are engineering plastics for specialized applications such as substitutes for metal in bearings, gears, cams, rollers, slides, door latches and thread guides in textile machinery. Nylon has an impressive list of suitable characteristics for these applications which include high tensile and impact strength, form stability at high temperstures, good abrasion resistance and self-lubricating properties. Nylon also provides a tough, abrasion-resistant outer cover to protect primary insulation on electrical wires.

#### Nylon 6

Nylon 6 has potentially as wide an application spectrum as nylon 66 but in the United States its utilization is approximately equally divided between resins and tire cord. At present, nylon 6 accounts for about 15 per cent of the nylon cord market. Its general use for clothing, carpeting and upholstery should increase with increased nylon 6 production.

#### Other nylons

The other nylons, both commercial and experimental, are not intended for general applications in competition with a less expensive nylon 66 and nylon 6. Their actual and potential applications are related to unique properties.

Nylon 610 is not jused extensively as a textile fibre but it has several properties which make it suitable for monofilaments to be used in brushes, sports equipment and bristles. These uses are related to the low moisture absorption of nylon 610 which results in a retention of stiffness and mechanical properties when wet.

Nylon 11 has been used in France as a textile fibre since 1955 but it has not been a commercial nylon in the

TABLE 7. FIBRE CONSUMPTION, IN BROADLOOM CARPETS, 1964 \*

Plane		Millions of pounds	Per cent
Weel		145	42
Nylon stepto		25	7
Nylon filament		100	20
Aarylic (+ modacrylic).		65	19
Cellulosic.		5	1
Cotton,		5	1
Polypropylane.	· · · ·	5	1
	TOTAL	359	100

Prom Chronical and Engineering News, 17 Petersney 1966, p. 33

United States. The uses of nylon 11 are generally related to its low moisture absorption.

The other nylons produce fibres which do not differ greatly from nylon 6. Nylon 7 is said to have better resistance to treatment with hot water and thus should have better wash-and-wear properties than either nylon 66 or nylon 6.

#### MONOMER SYNTHESIS

The discussion of monomer synthesis is concerned primarily with the synthesis of adipic acid and hexamethylenediamine for nylon 66 and caprolactam for nylon 6. The synthesis of monomers for other nylons is mentioned briefly.

#### Nylon 66

Although the syntheses of the two monomers for nylon 66 are to some extent interrelated they are discussed separately.

#### Adipic acid

Adipic acid is produced from benzene by at least four different routes. (2, 3)

- 1. Phenol is hydrogenated to cyclohexanol which is converted into sdipic acid by catalyzed nitric acid oxidation.
- Cyclohexane is oxidized by nitric acid to a mixture of adipic acid and nitrocyclohexane. The nitrocyclohexane may be converted to cyclohexanone oxime which is subsequently hydrolyzed and oxidized to adipic acid. It also may yield caprolactam by a reduction-dehydration process.
- Cyclohexane is oxidized by air to a maxture of cyclohexanol and cyclohexanone and this mixture is oxidized to adipic acid by nitric acid.
- Cyclohexane is oxidized by air to a mixture of cyclohexanol and cyclohexanone which is then air oxidized to adipic acid.

These various routes to adopt acid along with the commercial routes to hexamethylenediamine are shown in figure 1.

#### Cyclohexane

Three of the four important commercial processes for the production of adipic acid are based on the oxidation of cyclohexane. The cyclohexane comes largely from the hydrogenation of benzene although some is obtained from refinery streams. There are many methods by which benzene may be hydrogenated to cyclohexane and Haines has discussed the most important of these along with cyclohexane utilization. (3)

Cyclohexame can be oxidized directly to adlipic acid but most commercial operations use two-step processes involving nitric acid. (4) In the first step cyclohexame is oxidized with air to a mixture of cyclohexamel and cyclohexamone. In the second step the mixture is oxidized to adlipic acid. A typical process is shown in figure II. The cyclohexame is oxidized with air in the presence of a cobalt naphthemate estalyst and aestic anhydride or aestic acid. (5) The reaction temperature is constrolled between 120 and 200°C (usually ca. 155°C) and the pressure is maintained at about 75 to 150 psi. From 5 to 12 per cent of the cyclohexane is converted to give a mixture of cyclohexanol and cyclohexanone in a 65 to 85 per cent yield. This mixture is treated with five parts of 60 per cent nitric acid solution containing 0.2 per cent ammonium metavanadate plus copper turnings. The temperature is held at ca. 80°C. A 90 to 93 per cent yield of adipic acid is reported.

A key step in this process is the oxidation of cyclohexane to a mixture of cyclohexanol and cyclohexanone and control of the product ratio. (6) The composition of the mixture is not especially important when the second oxidation step is by air, a mixture rich in cyclohexanone is preferred. A recent process is said to permit close control over a cyclohexanol-cyclohexanone ratio by causing the oxidation to take place at a temperature between 130 and 135°C using cobalt naphthenate as the catalyst. The resulting mixture is then air oxidized to adipic acid with salts of copper and manganese as the catalyst. The over-all oxidation process is characterized by high yields at low operating costs and low capital investment. Another advantage is freedom from handling nitric acid.

The low conversion of cyclohexane, the many byproducts and the varying proportions of desired products have resulted in a large number of patented processes for the separation of recycle cyclohexane, by-products and the cyclohexanol-cyclohexanone mixture. It seems generally accepted that the oxidation process remains largely an art, while the various separation processes have been patented.

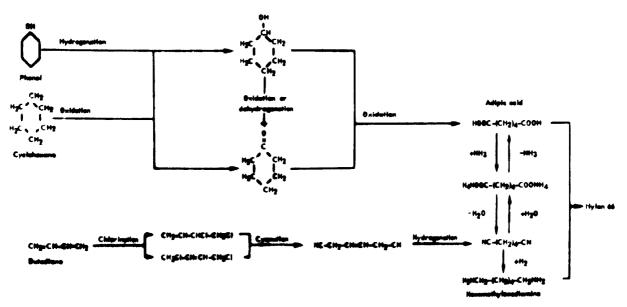
Both distillation and extraction techniques are used to separate the oxidation products. A fractional distillation process developed by Badische employs progressively lower pressures, first to separate cyclohexane, then the impurities, and finally the cyclohexanol-cyclohexanone mixture under a vacuum. (7) A steam distillation process is used in a process developed by Stamicarbon. (8) Steam distillation has the added advantage of hydrolyzing the esters of cyclohexanol and organic acids in the oxidation mixture. Steam also is used, with additions of alkali, in techniques claimed to have the combined effect of distillation and saponification of the esters in the reaction mixture. (9)

It appears that extraction techniques are also used in the commercial processes offered for license by Scientific Design and Inventa. The Inventa process first recovers free cyclohexanol-cyclohexanone from the primary oxidation mixture by straight distillation and then, in additional step, recovers the cyclohexanol which is present in the form of esters. (10) It does this by steam distillation plus alkaline extraction with the hydrotrops such as sodium xylene sulfonate or sodium toluene sulfonate. In the Scientific Design process the oxidation mixture is washed with a dilute alkaline-saturated salt solution to form an oil phase containing cyclohexanol and cyclohexanone and an aqueous phase containing the acids and sharply reduced amounts of dissolved cyclohexanol and cyclohexanone. (11)

# Cyclohexanol and Cyclohexanone

Cyclohexanol and cyclohexanone are usually produced as a mixture by the oxidation of cyclohexane and this mixture is converted to adipic acid without separation. The cyclohexanol in the mixture can be converted to cyclohexanone by passing the mixture over a zinc oxide catalyst. (12, 13) Relatively pure cyclohexanol is obtained by palladium catalyzed hydrogenation of phenol at 150°C and 50 psi.

A one-step process to obtain cyclohexanone from phenol has been patented in which gaseous phenol is mixed with hydrogen and passed over a palladiumcontaining catalyst at ca. 190°C with an inert gas as



Plane L. Parlow review to adpir and and honomethylonodiumine

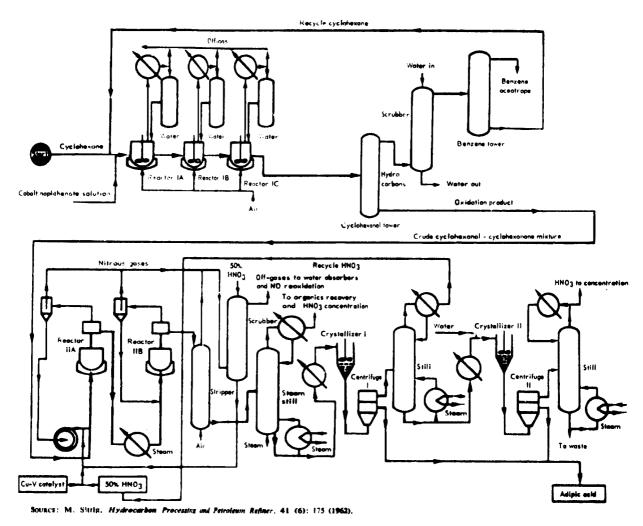


Figure 11. Two-stage process for the oxidation of cyclohexane to adipic acid by use of air for the first stage and nitric acid for the second stage

a diluent. (14) The product is rich in cyclohexanone (63 wt. per cent yield) and poor in cyclohexanol which decreases materially the necessity of dehydrogenating cyclohexanol to cyclohexanone. Palladium (5 per cent) on charcoal in the liquid phase at 120-128°C for 20 to 40 hours will give a 99 per cent yield of cyclohexanone based on a 62 per cent conversion of phenol. Cyclohexanone based on a 62 per cent conversion of phenol. Cyclohexanone is also reported to be obtained by the hydrolysis of nitrocyclohexane. (15) The nitrocyclohexane is a byproduct of the nitric acid oxidation of cyclohexane.

# **Hexamethylenediamine**

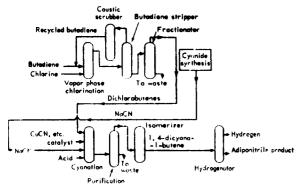
Hexamethylenediamine may be produced by the hydrogenation of adiponitrile over a supported cobalt catalyst at 100 to 135°C and 10,000 psi. The adiponitrile is produced from adipic acid by way of its ammonium salt (figure I) and from butadiene through a series of reactions which have not been given wide publicity in the literature (figure III). (16, 17) An electrolytic process has recently been developed for the conversion of acrylonitrile to adiponitrile. Another recent development is the conversion of a cyclohexanol-cyclohexanone mixture to caprolactone which is subsequently converted to hexamethylenediamine by reductive ammination.

Butadiene. The production of adiponitrile from butadiene is conveniently divided into two separate processes: (1) chlorination of butadiene and (2) cyanation of dichlorobutenes.

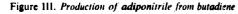
Chlorination of butadiene. The liquid phase reaction between butadiene and chlorine takes place readily at low temperatures to give good yields of a mixture containing 3,4-dichloro-1-butene and *trans*-1,4-dichloro-2-butene.

$$2 (CH_{a} = CH_{c}CH = CH_{a} + CI_{a}) \rightarrow CH_{a} = CH_{c}C$$

Industrial interest, as indicated by the patent literature, has been centred on the vapour phase reaction (figure 111). (18) Temperatures which appear in patents range from a low of 25°C (19) to a high of *ca*. 500°C.'(20) It is customary, however, to use a temperature in the range of 150 to 350°C. (21, 22) A typical product distribution for a reaction at 310°C and a 2 to 1 mole ratio of



SOURCE: J. C. Hillyer and P. S. Stallings, Petroleum Refiner, 35 (12):157 (1956).



butadiene to chlorine in the presence of nitrogen is in table 8.

The reaction also may be carried out in the presence of solid material such as coke (23) or in the presence of an inert gas (carbon dioxide). (24) It is also possible to obtain the same products by use of cupric chloride supported on pumice as the chlorinating agent. (25)

 $CH_{1} = CH-CH = CH_{1} + 2CuCl_{1} \rightarrow C_{4}H_{4}Cl_{1} + Cu_{1}Cl_{1}$ 

The product distribution for the reaction at 200°C is in table 8.

Cyanation of dichlorobutenes. The dichlorobutenes may be cyanated by using either hydrogen cyanide or sodium cyanide to give 1,4-dicyano-2-butene.

$$C_4H_4Cl_3 + 2 HCN \rightarrow$$
  
NC--CH\_3---CH = CH--CH\_3---CN + HCl

TABLE 8.

PRODUCTS FROM THE REACTION BETWEEN BUTADIENE AND CHLORINE

	Per	cent
Compound	Unpacked tube, 310°C	CuCl <sub>1</sub> on pumice 220°C *
3,4-dichloro-1-butene	36.0	42
cis-1,4-dichioro-2-butene	17.0	15
Irans-1,4-dichloro-2-butene	43.0	41
Monochlorobutadienes	1.1	2
Trichlorobutenes	2.3	b
Tetrachiorobutanes	0.3	ð
Unidentified	0.3	Ð

\* R. P. Arganbright and W. F. Yates, Journal of Organic Chemistry, 27:1205 (1962).

Not reported.

The reaction is catalyzed by a cuprous cyanide complex. (26)

The presence of 3,4-dichloro-1-butene is not a disadvantage because under the cyanation conditions it undergoes allylic rearrangement to yield 1,4-dicyano-2-butene.

$$CH_1 = CH$$
—CHCl —CH<sub>2</sub>Cl · 2NaCN →  
NC—CH<sub>1</sub>—CH CH—CH<sub>2</sub> CN · 2NaCl

The two geometrical isomers (cis and trans) of 1,4dicyano-2-butene are formed. One of these isomers (trans) is a solid and for ease of handling it is partially isomerized to a liquid isomer. (27)

$$NC--CH_{2}-CH = CH --CH_{2}CN \rightarrow NC--CH_{2}-CH_{2}-CH = CH--CN$$

The mixture is hydrogenated to adiponitrile in a vapour phase reaction over a palladium catalyst at 300°C. (28)

$$\mathsf{NC-CH_{9}-CH} = \mathsf{CH-CH_{9}-CN} + \mathsf{H_{9}} \rightarrow \mathsf{NC-(CH_{9})_{4}-CN}$$

The adiponitrile is subsequently hydrogenated to hexamethylenediamine.

Acrylonitrile. The most recent method for the production of adiponitrile involves the electrolysis of a concentrated solution of acrylonitrile in aqueous tetraethylammonium *p*-toluene solfonate at lead or mcrcury cathodes.

$$2CH_{1} = CH - CN \rightarrow NC - CH = CH - CH = CH - CH + H_{1}$$

$$NC - CH = CH - CH = CH - CH + 2H_{1} \rightarrow$$

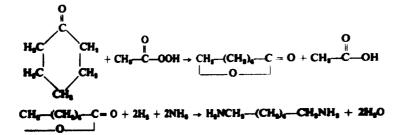
$$NC - CH_{1} - CH_{2} - CH_{2} - CH_{2} - CH_{3} - CH_{4$$

At controlled pH, yields are virtually quantitative at current efficiencies of close to 100 per cent.

This process is said to yield hexamethylenediamine at a much lower cost than processes based on either adipic acid or butadiene. One company (Chemstrand Division of Monsanto Company) is building a 40 million pound per year plant to utilize the acrylonitrile-to-adiponitrile process and other companies are active in research in this area.

It is also said that the same electrochemical technique can be used to prepare many different chemicals of many different classes.

Cyclohexanol-cyclohexanone. It is reported that a process has been developed whereby the cyclohexanolcyclohexanone mixture obtained during the production of adipic acid from cyclohexane can be converted to hexamethylenediamine. The alcohol-ketone mixture is treated with peracetic acid and caprolactone is formed. The caprolactone is converted to hexamethylenediamine by reductive ammination.



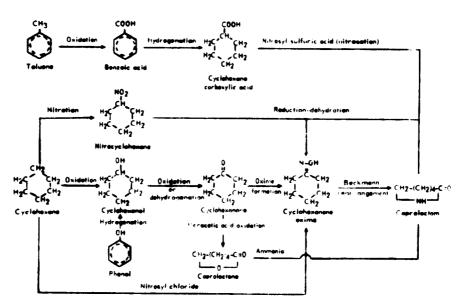


Figure IV. Various routes to caprolactam

# Utilization of intermediates

It is important to consider other uses for the intermediates in a chemical process. The ability to utilize an intermediate for some other purpose may be the factor which determines which of several processes will be the most attractive. Unfortunately, the intermediates produced in the current methods for the production of nylon 66 have very little utilization outside of nylon production.

Cyclohexanol. Cyclohexanol is used as a solvent in the synthesis of plasticizers and esters and it is used as an intermediate in the production of cyclohexanone, cyclohexylamine and phenol. Cyclohexanol is potentially cheaper than oxo alcohols and may become an important plasticizer alcohol. It is used to a small extent in the textile industry as a stabilizer and homogenizer for soap and synthetic detergent emulsions.

Cyclohexanone. Cyclohexanone is used as a solvent as well as an intermediate for the production of caprolactam for nylon 6.

Adipic acid. A small amount of adipic acid is used as an intermediate for the production of plasticizers, urethane resins and synthetic lubricants. Adipic acid is also used as a acidulent in foods and it has potential in dyes, metallurgy and insecticides.

Adiponitrile. Apparently the only utilization of adiponitrile is in the production of hexamethylenodiamine. Hexamethylenediamine. The only use for hexamethylenediamine is in the production of nylons.

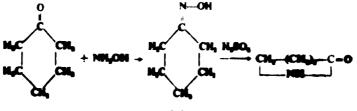
Caprolactone. Caprolactone can serve not only as an intermediate for hexamethylenediamine but also for caprolactam. A polyester of caprolactone is thought to be one of the ingredients in a new spandex fibre produced by Chemstrand.

#### Nylon 6

There are four industrial processes for the formation of caprolactam from cyclohexane, one from phenol and one from toluene (figure IV). Five of these processes are currently in use and the other process may be in operation at this time.

# Cyclohexanone oxime

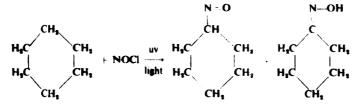
The production of cyclohexanone from *phenol* through cyclohexanol as the intermediate has been noted previously. The synthesis of cyclohexanone from *cyclohexane* also has been noted. The next step in the production of caprolactam is the formation of the oxime of cyclohexanone by treatment of the ketome with hydroxylamine sulfate at *ca*. 95°C. The oxime is converted to caprolactam by a Bockmann rearrangement catalyzed by an acid such as sulfuric acid (elsum) (29) or boric acid. (30)



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Another approach to the synthesis of cyclohexanone oxime and caprolactam is through *nitrocyclohexane*. The nitrocyclohexane is obtained by the nitration of cyclohexane (31) or as a by-product of the nitric acid oxidation of cyclohexanc. Caprolactam is produced directly by reduction-dehydration in the presence of borophosphoric acid catalyst. (32) The oxime of cyclohexanone can be formed by a palladium catalyzed reduction in the presence of lead or its compounds (33) at 140°C and at 500 psi, and by partial reduction over a zinc-chromium catalyst.

Nitrosyl chloride (NOC1) will react with cyclohexane under the influence of ultra-violet light to yield cyclohexanone oxime. (34)



The oxime can be rearranged by sulfuric acid to caprolactam without separation from the reaction mixture. The necessary sulfuric acid is available from the reaction between nitrosyl sulfuric acid and hydrogen chloride to form the nitrosyl chloride.

$$NOBO_{4}H + HCI \rightarrow NOCI + H_{1}SO_{4}$$

The nitrosyl sulfuric acid is produced by the reaction between dinitrogen trioxide and oleum.

# Caprolactone

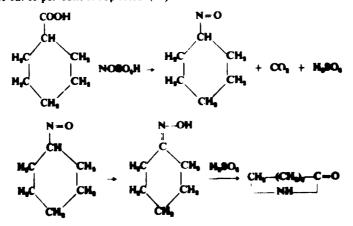
A recently developed process for the production of caprolactam has caprolactone as the intermediate. (35) In this process cyclohexanone is oxidized to caprolactone by peracetic acid in an inert solvent such as acetone at 30 to 40°C. A yield of *ca*. 85 per cent is reported. (36)

A modification of this process incorporates the *in situ* production of peracetic acid by use of a metal catalyst (cobalt or manganese is preferred), oxygen and acetaldehyde. A yield of 77 per cent is reported. (37)

Caprolactone can be converted to caprolactam by treatment with ammonia and water at 400°C. (38) An over-all yield from cyclohexanone to caprolactam of 65 to 70 per cent is reported.

# Cyclohexane carboxylic acid

Caprolactam can be obtained from cyclohexane carboxylic acid without the formal synthesis of the oxime of cyclohexanone. (39) Cyclohexane carboxylic acid is nitrosated with nitrosyl sulfuric acid in the presence of sulfuric acid at 55 to 65°C. Caprolactam is formed with the evolution of carbon dioxide.



Cyclohexans carboxylic acid is produced by the oxidation of tolusne to benzoic acid followed by hydrogenation of the benzoic acid to the cyclohexane carboxylic acid.

#### Other sylens

Nylon 610, mylon 11 and nylon 12 are commercial products and mylons 3, 4, 5, 7, 8 and 9 are being studied extensively with several of them is pilot plant and development stages. Their future is intimately associated with the cost and availability of their monomers. With the exception of sylon 610 (sebacic acid, hexamothylenedismine) two general types of monomers are used for the synthesis of these sylons: emege amino acide  $[H_sNCH_r(CH_s)_{sr}-COOH]$  (40) and lactame. (40, 41)

# Nylon 610

The fusion of sodium ricinclents (from castor eil) with 70 per cent sodium hydronide produces enpryi alcebol and disodium sobnests.

The free sebacic acid is obtained by acidification with a mineral acid.

# Nylon 11

11-aminoundecanoic acid is produced commercially from castor oil which is primarily a mixture of the triglycerides of ricinoleic, oleic, palmitic, stearic and dioxystearic acids. The triglyceride of ricinoleic acid predominates in this mixture and it is the precursor of 11-aminoundecanoic acid.

The mixture of glycerides is treated with methanol to form the methyl esters of the acids originally present as glycerol esters. Methyl ricinoleate is separated and pyrolyzed to give *n*-heptaldehyde and methyl  $\Delta^{10}$ -undecylenate.

The methyl ester is saponified and 11-bromoundecanoic acid is formed by the peroxide catalyzed addition of hydrogen bromide to the terminal carbon-carbon double bond.

$$CH_{g} = CH (CH_{g})_{g} - COOH + HBr - ...$$

$$BrCH_{g} - (CH_{g})_{g} - COOH$$

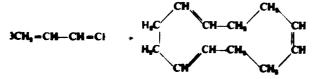
This reaction is the key to the process. It is caused to take place in a packed column reactor through which flows a solution of the organic acid in a toluene-benzene solvent. The hydrogen bromide is introduced along with air as a countercurrent gas stream. Approximately 96 percent of the resulting bromide is the 11-bromo isomer and 4 per cent is the 10-bromo isomer. The amino acid is formed by the reactor between the bromo acid and ammonia.

$$BrCH_{g}$$
 ( $CH_{g}$ )<sub>g</sub> COOH +  $3NH_{g}$  +  $H_{g}NCH_{g}$  ( $CH_{g}$ )<sub>g</sub> COONH<sub>4</sub> +  $NH_{a}Br$ 

The organic acid is obtained from its ammonium salt by acidification with a mineral acid.

# Nylon 12

Three molecules of butadiene can be cyclized to 1, 5, 9-cyclododecatriene (42) which can then be converted to lauryllactam. (43)



The hydrocarbon may be epoxidized with peracetic acid or acetaldehyde peracetate. The epoxide is hydrogenated and the saturated epoxide is rearranged to the ketone with magnesium iodide at 100°C. (44) The oxime of this ketone is then rearranged to lawryllactam.

# **POLYMERIZATION**

The nature of the monomer determines the type of polymerization. The reaction between a diamine and a dicarboxylic acid is a simple condensation caused by the elimination of a small molecule (water). The polymerization of *omega* amino acids is also of this type. Condensation polymerization proceeds by step reactions and has the following characteristics. (45)

(a) Any two molecular species present may react.

(b) The monomer disappears early in the reaction.

(c) Polymer molecular weight rises steadily throughout the reaction.

(d) Long reaction times are essential to obtain high molecular weights.

(e) At any stage all molecular species are present in a calculable distribution.

Initial molecular weight control is obtained by stopping the reaction at the desired point. Subsequent heating, however, may cause a change in molecular weight. This situation can be avoided by using slightly less of one bifunctional reactant or by adding a small amount of a monofunctional compound. The molecular weight stabilization of nylon 66 by acetic acid is an example of the latter method.

Lactams may be polymerized by a typical step reaction preceded by a ring opening reaction. The ring opening step is stoichiometrically an addition reaction followed by a typical condensation polymerization. Lactams also may be polymerized by a mechanism which involves ring opening induced either catalytically or by the presence of a small amount of an end-group-forming substance. The polymerization of caprolactam in the presence of a small amount of water is typical.

Polymerization of this type resembles chain polymerization because it proceeds by the addition of monomer to the growing molecule. It differs from a typical chain reaction, however, in respect to the reaction kinetics because the chain-initiating step and the subsequent addition steps are similar and proceed at similar rates. The polymer molecules continue to increase in molecular weight throughout the reaction. In stepwise ring-scission polymerization, all the chains are initiated at the same time and grow for the same length of time. The distribution of molecular weights is consequently very narrow. (46)

Lactams also may be polymerized by ionic chain mechanisms. (47, 48) This type of polymerization is a true chain reaction with an initiation step, a very rapid propagation step and a termination step.

#### Vy**lon 66**

The polymorination of hexamethylenodiamine and adjule acid to sylon 66 is a relatively simple process. The salt of the diamine and acid is dissolved in water and added to an autoclave along with 0.5 to 1.0 mole per cent acetic acid. The temperature is raised to  $270-280^{\circ}$ C at 250 psi. The pressure is then reduced to permit the removal of water. After a total time of 3 to 4 hours, nylon 66 is extruded as a ribbon by nitrogen pressure through a bottom valve of the autoclave. (45)

# Nylon 6

Caprolactam is converted to the omega amino acid by adding water to open the ring and the omega amino acid is then polymerized at elevated temperatures (230-280°C). (49) The polycaprolactam is in equilibrium with about 10 per cent of the monomer at 280°C. (50) This monomer may be removed by washing with water or by the use of a vaccum.

Reduction of monomer and low molecular weight polymer content in polycaprolactam resin is one of the most serious problems in nylon 6 production. Low temperatures favour high polymer homogeniety but reaction times are excessive. Activators (cocatalysts) such as water, acids, amine salts and alcohols tend to stabilize the polymer at low molecular weights. The rate of depolymerization is directly proportional to reaction temperature and water content. It is reported that the Russians have a continuous and rapid process based on the use of sodium that is essentially free of these difficulties. (50, 51, 52)

#### Nylon 610

Nylon 610 is produced in a manner similar to that used for nylon 66.

#### Nylon 11

Nylon 11 is formed by the simple heating of the monomer in a water suspension. (53) The suspension is fed into a three-compartmented reaction column. The monomer melts in the first compartment, much of the water is removed, and polycondensation begins. The condensation continues in the second compartment and the desired degree of polymerization is obtained in the third compartment. The third compartment also served as a reservoir for the spinning process.

# Nylon 12

The polycondensation of lauryllactam can be carried out in the melt in the presence of water or salts that liberate water. (53) The polymerization of lauryllactam is slower than for caprolactam but thermal stability of lauryllactam permits the use of higher temperatures to assure an adequate polymerization rate.

#### SUMMARY

From the foregoing discussion of nylons it is apparent that only nylon 6 and nylon 66 should be considered for production in a developing country. The prime reasons for this are the entaneive technology available for the production of these nylons and the low cost of the rew materials. The question as to which nylon — nylon 6 or nylon 66 — is more difficult to answer

The decision as to which nylon is the one to produce cannot be made on the basis of one being markedly superior to the other in respect to properties. One large producer of nylon 66 states that the two nylons are "indistinguishable" by the consumer of most finished products. Producers of nylon 6 may not agree Certain generalizations can be made, however, in respect to production and processing.

It is generally conceded that nylon 6 production requires less capital investment and nylon 6 fibres are easier to spin. Nylon 6 is also said to be less costly to produce. This is difficult to assess. The large number of different processes available for caprolactam production indicates that no one process is sharply superior to the others. The choice of process will be dictated by other considerations and there should be one process bestsuited to the raw material and by-product situation of each country.

All the processes for the production of caprolactam which have cyclohexanone oxime as an intermediate will produce ammonium sulfate as a by-product. This would be desirable in a developing country because of the use of ammonium sulfate as a fertilizer. The caprolactone process has acetic acid as the by-product and acetaldehyde as the raw material in addition to cyclohexane (or phenol). This process should be considered if there is a need for acetic acid. The process starting with toluene does not appear to have any outstanding advantages over those based on cyclohexane (benzene).

The final decision as to which nylon and which process must be based on a careful study of all factors which are applicable to the particular country. It is my opinion that nylon 6 will be the most desirable nylon for most countries and the most desirable process for its production will be one which produced ammonium sulfate as a byproduct. The nitrosyl chloride process for the production of cyclohexanone oxime appears to be the simplest from the standpoint of the number of chemical transformations involved and its proponents claim a distinct cost advantage over other processes.

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# **a geowth of plantics in developing countries**

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#### INTRODUCTION

The objective of any developing country must necessarily be to provide the citizens an opportunity to had a life with all basic amenities such as food, clothing and housing.

In order to provide these basic amonities the planmig of the developing country has also to be orientated towards industrialization as it is industry that provides directly or indirectly time bonefits to the action. Plastics because of their versatility of application have firmly linked themselves with the growth of industry and standards of living. So extensive is their use that it is not possible to conceive of a community without plantics in fact the consumption of plastics in a country is becoming to be acknowledged as an index of its economic advance.

Thermoplastics account for about 70 per cent of the world consumption of plastics today. The table below gives the production and percentage of thermoplastics in some of the developed countries in 1963.

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bialized Bearies		United Ministern		Japate	
Reality	**	<b>76.</b> ##	3. B	<b>Fit.</b> 49 <b>F</b>	*
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196	7	19	4	95 348	52
Ĩ	24	17	15.5		10
<b>520</b>	19	76	15	32	5
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	765 195 595 680 590 2,761 3,680	705 30.5 195 7 975 24.5 080 24 980 19 2,704 3,000	Rk.Her         %         Rk.Her           106         20.5         147           106         7         19           506         20.5         155           610         26         17           500         19         76           2,701         404           3,600         737	The         30.5         107         34           156         7         19         4           506         24.5         195         34.5           600         24         77         15.5           500         19         76         15           2,704         404         3,000         797	The set of the set of

The demand for thermospherics with special reference to pulpethylons, PVC and pulyetyrons in developing constraint, the factors governing their growth and the effect of this goverth on subification of a nation's contently from the subject of study in this report.

# Barrupy of unpurture in Indea

The Schwarzing of and products from imported plastic meaningle marked the baginning of the plastics industry in India. As the mean-future of plastics grads increased during the last decade, the domand for the meanifesture of the last scale, was full.

As present une formalisierte, planet formalisierte, pripaligium, PVC and pripatyruse are bring manyfastured and are to a large extent meeting the current demands. The local conditions and the various factors that have suffaseneed the industry in the field of polyotherium and PVC need a close study.

The first polyathylene plast with a capacity of 3,550 tensymmetric based on abohol was set up in 1959. At the time of its planning, alothol from molasses, a by-product from the sugar industry, was available in planty. The product polyathylene was available at a high price due to the low experity of the unit and the price of the new merovial. This confined its use to the field of only " eccentric!" applications such as film for packaging. For communer peek, its acceptance was restricted. The account plant, also based on alsohol was duried in 1958. The present total installed expending is always 11,050 templantum. However, alsohol on a raw material has been in short supply since the establishmont of a large synthetic rubber unit based on it. This shortage has restricted the production of polyethylene to the extent that even the present demands are not met and the polyethylene is being imported.

The first unit with an annual capacity of 3.6689 tons for manufacture of PVC in the country was based on wetylene from carbide PVC afforded an outlet for hydrochloric acid which is surplus in the country and has been affecting adversely the growth of the caustic ands industry by its disposal problem. The second unit with an annual capacity of 7,000 tons also based on acetylene from carbide was started in 1964. The document for basing these two factories on carbide was influenced by the availability of reasonably priced power in sufficient quantities at that time and also the non-availability of petroleum based raw materials. Moreover the manufacture of PVC from ethylene has had the problem of dispusal of the by-product hydrochlonic acid and the manufacture of asstylene from potrochemical sources had not been perfected. Due to the high cent of manufacture on account of low grade raw materials and increasing power costs, and restricted power availability prospects of growth of the PV. industry based on calcium carbide are block

The first petrochemical complex, with a capacity of 20,000 tons of polyethylene and 20,000 tons of PVC has been planned to come into production in early 1967.

# PATTERN OF END USER

The applications of plastics can be generally divided into two types

# 1 Industrial

In applications that take advantage of sertain special properties of plastic materials. These applications comprise chiefly electrical insulation, moisture and asid/ alkali proof protective material in packaging of a variety of essential commodities, pipes and results for the chemical industry and in plant mulching in agriculture.

As substitutes for conventional materials, for industrial and domestic use such as pipes, material of construction. in furniture, upholotory, moulded goods, floor tiles.

#### 2. Direct consumer articles

The pattern of end product usage of polycthylans, PVC and polystyrons in developed soundries is as fullows.

#### TABLE 2

······		ii.	
3. Industrial			
Substitute . Special applications	)H ]D	<b>56.8</b> 36.1	26.6 46.6
1. Direct communer	*	12.1	

The entent to which each type of application finds use is dependent upon the general economic status of the country and the prices at which plustics are available.

In a country with a developing economy, the prices of plastics are necessarily higher initially than those prevalent in fully developed countries due to low capacity production units and non-availability of cheap raw materials. The higher prices will be a discoursiging factor in widening the sugge/applications of plastics. The actual usage will thus be limited to applications where the special properties of the plastic are utilized, which in furn are vital to the development of the economy.

In India the stream on the usage of plantics will be on special applications and as the price of the plantics goes down, the applications of plastics as substitutes to existing materials will increase. The increase in the domand for plastics for direct consumer products will depend upon the price of plastics and the increase in per capital moome. Taking all these into account, it is estimated that the pattern of end uses of plantics in India will be as follows.

F		-	1
	-		• •

		Polyestastasta Por casa	PVc Par can	Polyasynake Per odda
١	Industrial			
	Substitute	25		25
	<b>Special application</b>			
2	Direct communer	25	10	25

#### EDTHIATE OF DUMAND IN INDIA

Industrial development of a usuatry is the most important factor in determining the domand for plastice, the other factors being influential in quickening or retarding the rate of growth of the industry

The potential domand of plastics by 1971 has been worked out by two independent methods

# (i) On the basic of par capita consumption

The per capite concumption of visel can be taken as an index of industrialization of a country. The per capite concumption in 1953 in India and some of the developed countries is given bylew.

-			
- ¥	-	а.	

Ø		Per annia spat
		ammungiden (Ap)
		and the second second
Paderal Republic of Quera		585.0
United States	•	
		<b>SDI.0</b>
United Kingdom		468.0
Australia		
		346.0
Phone		386.0
-	•	
Japan		386.0
		M A
	×	<b>96.4</b>

The projected demand for steel in 1978-71 is 20 million tons. However taking a conservative figure of 14 miltion tons, the per capital consumption will be 26 kg, which is still only 5 per cent of the present figure in advanced countries. This figure can be used to work out the demand for plastics.

The por capital consumption of plastics in India was only 0.67 kg in 1962 and as against this the consumption in developed countries in the same year was as given in the following table.

Per capita commention of plastics as in 1962

FABLE 5

( cutter v	Per capita. plantes consumption the
Poteral Republic of Germany	<b>10</b> .2
United States	18.0
Sweden	14.4
hapan	12.0
United Kingdom	10. i

This shows a per capite consumption of about 16 kg in advanced countries. Taking special applications as 40 per cent, the per capite consumption of plautics for special applications is 6.4 kg. In India: therefore, the corresponding per capite consumption will be 5 per cent of 6.4 kg, which is 0.32 kg. Because of higher prices in India: the percentage of plastics devoted to special applications is especial to be 50 per cent instead of 40 per cent as in advanced countries. Therefore, the total per ceptie demand can be expected to be 10.64 kg which corresponds to a total consumption of 345,800 tons per ansum

#### (18) Dy estimation of domand of end products

The major industrial outlots of polyothylone and PVC are films for packaging, cable/wire insulation and pipes and shoets for industrial application. The forecast of the domand for the above applications can be made by a study of the provith of packaging requirements for fortilizers and other commodities, power generation and distribution and the charging industry.

# Requirement for insulation

The use of plastes as mendation material for vives and cellins was started in 1960. Due to the restricted availability of row material the consumption of plastics for vives and orbits was only 300 tunnes in 1961 and it is new expected that the consumption will be 5,000 tons in 1966, a two-fold increase. During the same period the power generation will measure from 5.7 million kW to 12.75 million kW. The power generation is expected to be 20 million kW by 1970. In order to meet the domand for the distribution of the power and also to meet the requirements of telephone industry, it can be estimated that the domand of plastes for this appleation also will be of the order of 20,000 tons.

#### Requirement for packaging

Plastic films are used for packing fertilizers, chemicals, food, textiles etc. The requirements of plastics for fertilizer packaging can be estimated by the production of fertilizers which is estimated to be of the order of two million tons of nitrogen and one million tons of P.O. by 1970. Taking an average requirement of 100 bags per ton of nitrogen and P.O., the total requirement of plantics for packing fortilizers will be 60,000 tons. assuming only 30 per cont of the fertilizers produced are pucked in plastic lined bags. This estimate is based on the use of plastic-lined bags. However, the present trend in developed countries is to use exclusively plastic hags for packing fertilizers to bring down the cost. As the method of handling improves in India and the price of plastics comes down, it will be possible to use plastic bags exclusevely. This will further increase the demand of plastics for packing fertilizers.

The requirement of film for packing textiles chemicals and food articles can be assumed to be 50 per cent of the plastic requirement for packing fertilizers on a conservative basis

Thus a total 40.000 tons will be required for packaging.

# Requirement for pipes and vessels

The use of plantic pipes and special lined vessels has come up in India very recently PVC pipes are now being used for handling wet chlorine, hydrochloric acid, purified water brine, caustic soda and other chemicals. Even the existing caustic soda units using rubber lined/ commic pipes are changing over to PVC pipes. It is very difficult to estimate the demand for this end use. However, it can be assumed that the total demand for plastic pipes for all purposes will be of the order of 20,000 tens by 1970.

#### Requirement for leather cloth

The present consumption of PVC for leather cloth manufacture is 4,000 tons, annum 30 per cent of this commodity is being exported. With the free availability of PVC resin at cheaper prices it may be assumed that the domand will at least be three times the present consumption. Thus the domand may go up to 12,000 tons by 1970.

Thus the total consumption of plastics for these and uses will be as follows

Lonther electh	Par a	12,000
Pipes		3,00
Wires and califes		38,000
Plan for packaging		

The personage consumption of plastics surveyeds then and uses in various countries are given in the table ballow : TABLE 6

	Polyeshylme (United Kingdom)	PVC (Japan)	Palystyren: (United States)
Percentage of plastics consum- ed for			
Pilm for packaging	34.5	2.0	25
Wires and cables	3	i2	
Pipe	7.5	18	
Leather cinth		12	I
Τογάι	45	44	26

Since these are special applications, the percentages for India should be taken at 25 per cent more. From this the total demand of Polyethylene, PVC and Polystyrene can be worked out at 280,000 tons per annum.

As mentioned earlier, the thermoplastics form 70 per cent of the total plastics. Thus the potential demand will be of the order of 400,000 tons.

# FACTORS INFLUENCING RATE OF GROWTH

The estimate of demand that has been arrived at is a potential demand which will provide the basis for the growth of the industry. The actual rate of growth may be governed by the availability of raw materials, profitable outlets for by-products, the ability to produce plastics at a price which will stimulate demand at a rapid pace, the availability of plasticizers and chemicals, and the simultaneous setting up of units for processing plastics into end products.

In view of the limited financial and technical resources of a developing country, progress will also depend on the judicious choice of capacities, import of know-how and the quantum of exports for earning foreign exchange.

#### Raw material availability

The stimulation to the growth of the production and unage of plastics by the advent of petrochemicals and also availability of petrochemical feedstocks is tremendous. In Japan the production of ethylene based on petrochemical feedstock, which is an indication of the production of plastics, started in 1956. From a production of FOD.00D tons of ethylene in 1961, the same has increased to 340,000 tons in 1963. It is further expected that due to the latest expansion schemes the production in 1965 will ge up to 710,000 tons and one million tons by 1967.

In India with the discovery of crude oil in various locations and also the establishment of refinery capacities it is expected that by 1970 about 24.25 million tons of crude oil will be refined. The naphtha produced from this orade oil will be about 3.9 million tons. It is estimated that the gasoline demand by 1970 will be of the order of 1.4 million, having a surplus of 2.5 million tons of naphtha. Out of this it is espected that about 1.2 million tons would be utilized for furtiliar production and 1.3 million tons of naphtha will be available for petrochemical feedstocks.

Sixty per cent of the ethylene production is used for the manufacture of plastics in developed countries. Further, in view of the increasing use of ethylene for PVC due to the new development of the conversion of by-product hydrochloric acid into chlorine, the usage of ethylene to plastics in India will be of a much higher percentage and can be expected to be of the order of 75 per cent.

**Based** on the above, it is estimated that about 250,000 tons of ethylene will be available for plastics by 1970. This would be equivalent to production of approximately 350,000 tons of ethylene-based plastics per annum.

The other main raw inatenial for manufacture of PVC is chlorine. The demand of caustic soda has been increasing at a steady pace and is expected to be 600,000 tons by 1970-71. The growth of this industry is however, dependent on the utilisation/disposal of the hy-product chlorine as the utilisation of chlorine h s not yet progressed to the same extent in India.

With a production of 600,000 tons of caustic soda and assuming a 75 per cent utilisation of chlorine the total chlorine available will be 400,000 tons. Out of this quantity, it is estimated that 150,000 tons will be consumed by the pulp and paper industry and another 150,000 tons by chlorine-consuming industries including organic chemicals but excluding plastics. This will, therefore, leave a margin of 100,000 tons of chlorine to be consumed by the PVC industry in the plastics field. This will correspond to a production of about 140,000 tons per annum of PVC.

### By-product utilization

The setting up of an ethylene plant based on petrochemical raw material for the manufacture of plastics yields a number of by-products. The utilization of these by-products will pose a problem in the context of the economy of developing countries.

India has only just introduced itself to ethylene hased derivatives. It is a long way to realize the full utilisation of propylene, and butadiene derivatives. Even is Japan and America it is only very recently that propylene and other by-products from ethylene plants have started getting by-product values other than that of fuel.

We may consider the possibility of utilizing the byproducts from some of the othylone plants for the manufacture of nitrageness fortilizers which will be required in large quantities in the next few years in Indus. At a later stage once there is sufficient domand, utilization of these may be switched over to the manufacture of propyless, and butedione derivatives. The concequent higher byproduct value will reduce the cast of athylone. Manufacture of fortilizers can then be based directly on negleta.

# Effect of price on growth

The prices of plastics in India as compared to these in other countries are as follows:

TABLE 7 (Cents/kg)

	Plastic	United States	United Kingdom	France	Fed. Republic of Germany	India
PVC General purpose Polystyrene		35.2	34.7	38.7	35.0	106.2
General purpose Polyethylene		31.9	41.2	40.7	36.1	102.0
General purpose		38.0	51.5	45.7	44.2	151.0

It will be seen that the price is three times the price in developed countries. The cost of manufacture of plastics at present is high in India due to the small size of operations and high priced raw materials.

The prices of plastics in the United States have been continuously coming down as can be seen from the following table:

TABLE 8 (Cents/kg)

	1955	1980	/96./
Polyothyione	90	62	38
PVC	70	40	35.2
Połystyrene	62.6	48.5	

This decrease in the price is due to the installation of large-scale production units, better utilisation of byproducts of ethylene manufacture from petroleum sources and technological developments.

Similarly in Japan the prices of plastics came down very sharply after the manufacture of plastics was based on petrochemical technology. The price of polyethylene which was 121 cents/kg in 1956 when petrochemical based units were first installed has fallen to 49.2 cents/kg in 1963.

The effect of the price of plastics on plastics growth can be seen from making a study of the plastic goods in the United States. The per capite consumption of plastics in the United States rose from 15.4 kg in 1959 to 21 kg in 1963. During the same period the per capite consumption of steel had risen from 525 kg in 1959 to 500 kg in 1963. While the per capite consumption of steel has risen by only 10 per cent during the same period the per capite consumption of plastics rose by 36 per cent and this is mainly due to the reduction in the price of plasties which came down by 40 per cent while the steel prices remained.

The prices of plastics in ladia are expected to come down very repidly in the next few years as petrochemicalbased othylens will be available for plastics and the size of the units will be comparable to the units installed in the developed countries. It is haped that the plastics price will be 30 per cost of the process level and the instandous reduction in price will stimulate the use of plastics to a very grapt catent and new process of ecowill be developed. The and uses of plastics for substitution of conventional materials and also the consumer articles which find direct consumption will be very great.

The magnitude of the cost of plastics due to the change from the present raw material to the petrochemical-based units can be seen from the following tables where the material and utility costs of ethylene and vinyl chloride based on zleohol and carbide respectively have been compared with the corresponding costs from petroleum feedstocks.

Comparison of material/utilities cost per ton of ethylene from alcohol and naphtha

TAME 9

Ethylone from al	rahai	Ethylone from maphoha				
liem	Rs ran ethyione	ltem	Re/son erhydane			
Alcohol	530	Nuphtha	270			
Catalyst/chomicals	20	<b>Dy-product not back</b>	140			
Utilities and fael	70	Catalyst	110			
		Chemicali	15			
		Utilities				
	620		385			

Comparison of material/utilities cost per ton of vinyl chloride from carbide acetylene/naphta ethylene

TABLE 10

Pinyl chieride from c	arhide acetylene	Vispi chloride from saphtha ethylom						
ise an	Ne : son vine : cideride	hem	Ra Jan Vinyi chiavtai					
law material		Rew meterial						
Lime-stens	115	Naphila	135					
Charonal	125	By-products nor						
		bask						
Others	1.50							
	790		45					
Chiarine	250	Chiorine	390					
Catalyst/shorts	m 🗰	Catalyst/shomtoals	35					
Velilita	200	Velliges						
			- În					

# Availability of plasticizers and chemicals

PVC which will constitute a major portion of the total plastics demand requires special chemicals like stabilizers and plasticizers in order to convert the same into end products. Growth of these industries for the manufacture of these stabilizers and plasticizers also requires special attention.

# Units for processing plastics

The growth of manufacture of end products needs special attention as the consumption of 400,000 tons/annum from about 30,000 tons of present consumption will require a large number of units for and products to be installed.

# Choice of capacity

Whereas it is a well-known fact that the larger conseities will be more economical, the choice of capacity to be installed has to be tempered by consideration of the domand that can be created. It might be less economic to have a large capacity plant running at reduced capacity for a period of years because of inadequate demand, rather than installing lower capacity plant which is run at almost full capacity and expanded as the demand builds up. In view of this, large complexes if envisaged, should be put up in stages so that there is not too much essess capacity over demand.

In India six petrochemical complexes are being planned in the next few years. The end products to be manufactured and the capacities of each complex, will have to be desided after careful consideration.

A study of the capital requirement for a petrochemical complex shows that the capital cost of the end-product plants can contribute to over 90 per uset of the total capital investment. Hence the over-all consensity of a petrochemical project will be largely in the size of endproduct plants. Hence it will be more consomic to have a scheme with fewer but larger and-product plants than one with multiple products of small capacities. Hence with the setting up of vix petrochemical complenes a judicious allocations, of and products amongst the versue complexes will have considerable financial advantages. Duplication of end products will unnecessarily increase the over-all requirement of technical supervisory manpower.

It is evident from the above, that the size of a cracker by itself is not the final determinant of economy of production and its choice must be dependent on a careful selection of the number and capacity of end products to be made.

#### Import of know-how

Petro-homical technology is very recent and few have the experience of successful and continuous operation. Even Japan which has placed considerable stress on development of their own processes, have up to date relied on firms in Amorica for supply of ethylene and allied plants and know-how in their country. It is very important for developing countries to encourage import of knowhow in initial stages.

Know-how can be imported in various ways either by a bulk payment, or by royalty or by capital participation. The advantage of capital participation is that firms supplying the know-how are more actively interested in the development of the industry and supply know-how on a continued basis quite readily. It also serves to reduce the burden of foreign exchange to be obtained for a project.

#### Emphania on exporte

The ultimate stability of a country's coorseny is the balance of trade between imports and exports. The petrochemical inclustry is an entremely capital intensive industry. It is very constant that any planning of this industry should provide for export of 20-30 per court of the products to be made. In this way the capital required for the petrochemical industry will not be responsible for depletion of the foreign exchange reserves and chould in fact be used for carsing further amounts of foreign exchange which can be utilized for meeting other requirements. This export should be maintained even if it means componenting by a slightly higher despective price.

# 9. PLASTICS PROGRESS

# J. M. Goppol, Shell Internationals Research Mastachappij N.V., The Hague, Netherlands

#### INTRODUCTION

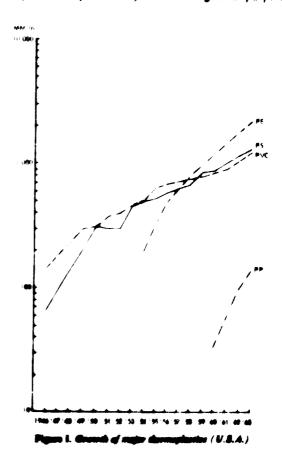
We live in a rapidly changing world, and these changes are primarily brought about by the tromendous efforts in research and development in nearly all fields of science and technology. Impressive progress has been made in the last docades, and the advent of electronic computers, the discovery of the hereditary code incorporated in the structure of the polynucleic acid molecules and, of course, the development of atomic energy, present significant examples. No loss spectacular are the developments of entirely new synthetic materials potentially affecting nearly every aspect of our daily life. Their history goes back to 1909, when Daockeland first synthesised from phenol and formaldohyde condensation products which after a difficult and slow start became accepted as stundard materials for e.g. insulation applications, which in turn have been a powerful stimulant to the development of the electrical industry. It is remarkable that, in spite of the many new synthetic materials which have emerged from the research and development laboratories, the phenolformaldehyde resins have still managed to keep their position

The next industrial developments in the polymer field took place in the thirties with the discovery of the industrial potential of polystyrone and polyvinyl chloride. substances at that time already known for about 100 years. but which had remained dormant, partly because of inadequate control of the difficult and at the time obscure ination reactions, partly because of a lack of ht into and equipment for the handling of such nals, and also because of a lack of interest on the urt of a world which although republy industrializwas still mainly committed to traditional materials ad oreformanchop. Porhaps the main factors which put an end to this period of dormancy were the success of the lobydo rossas, the recognition of their inhorent drowbashs in the processing sings and the remarkable ments of the in ue in the field te tool of Hasht mai ds. Thus, during the thirties, the interest in N AN a new class of synth ale a nulated, but it is fair to say that without er of additional factors we would not have seen n postwar period the trans wh have now led to revolutionary ch m in er nh of ind atry. We will attempt to an -116. AS 21000 AS AS alysis may, it is hoped, land to t on of limit mai of **1 a** a -----

industry should be briefly discussed, so as to define more closely the role of the new materials in our present technology.

# GROWTH OF THE PLASTICS INDUSTRY

The thermoplastics can be roughly and somewhat arbitrarily divided into two groups, next to the large category of "general purpose" plastics, we may distinguish a smaller group of special plastics which offer more specific properties, usually at a higher price. These materials, such as polyamides, polycarbonates, polyformaldehydes, are widely used for special, often industrial, applications where the higher price is no detertent, but this is a somewhat limited market and these materials have not had such an impact on the technical and economic pattern of present day life as the "general purpose"



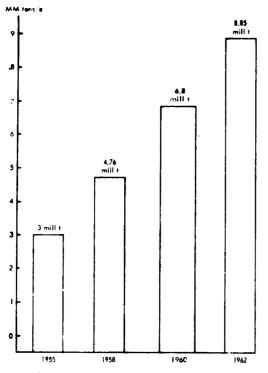
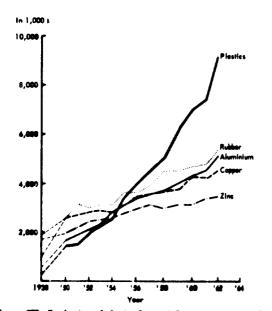


Figure II. World production of plastic materials

plastics, suitable for widely varying applications, available at low price and now being used on a tremendous and still-increasing scale. In discussing plastics growth we will mainly direct our attention to these "general purpose" materials comprising polyvinyl chloride, polystyrene and polyethylene. Polypropylene, also based on a generally available low cost monomer, might in time join this group, the growth of which is illustrated in figure I.



Pignes III. Production of plastics by weight in comparison with other

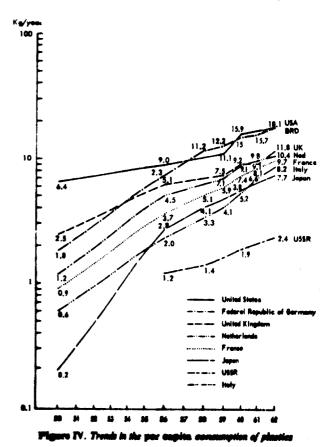
The world production of plastics increased very nearly threefold in a period of only seven years, from 1955 to 1962, in which period fast growth rates are observed in all areas, as illustrated in figure 11.

It is also of interest to compare the figures given with production data of other materials, in particular nonferrous metals. This comparison gives figure III, which shows that on a weight basis plastics have surpassed non-ferrous metals. The difference on a volume basis would be even more striking.

With such enormous production figures for the synthetic materials, the *per capita* consumption in the industrialized areas is, of course, also very high. It is highest in the United States as shown in figure IV, which indicates, as could be expected, that the use of plastics is associated with the level of economic and industrial development. The USA are the leaders, but the other areas are rapidly following. In fact, the impression obtained is that the time-lag in industrial development between the United States and e.g. European countries, which in the recent past was estimated at about fifteen years, is decreasing and may now amount to about five years. It would be most interesting to have information about this time-lag for other developing areas and particularly, to know how it might be reduced.

# **GROWTH FACTORS**

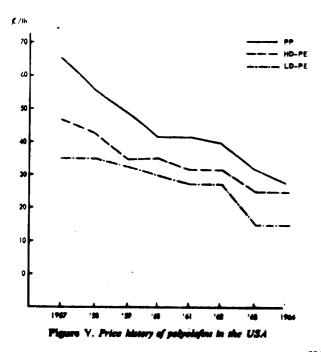
A number of factors have contributed to the impressive growth of the plastics industry as illustrated in the preced-



ing paragraph. In the first place the ready availability should be mentioned. This is coupled with the supply of base materials which can be based on petroleum, which constitutes a ready and flexible source of a number of intermediate chemicals producible at relatively low cost, provided that large production facilities are installed. Equally important in this respect is the close control over the complicated chemical processes converting the intermediate monomers into the plastic raw material. These polymerization plants, efficiently designed and operated, again on a large enough scale, enable the production of the plastic at relatively low cost. Consequently, plastics have become increasingly available at continuously decreasing prices, as is illustrated in figure V for polyolefins, but which also holds for other plastics. Figure VI shows that in contrast, the price of more traditional construction materials has been more or less constant. Such trends have been a powerful stimulant for the development of the subsequent plastics technology.

Potential low cost and availability in themselves, however, are not enough to ensure progress and success, and it may be of interest now to analyse what further factors have been operating in the recent past and have resulted in the plastics industry as we know it today. We believe that the more important ones are the following:

- 1. The inherent properties of the new materials, frequently giving them economic advantages over conventional materials;
- The consistent efforts on the part of manufacturers to promote the use of plastics materials, where technically and economically justified, by product and application development;
- 3. The readiness of the manufacturers of processing equipment to accept the challenge and construct appropriate machinery;



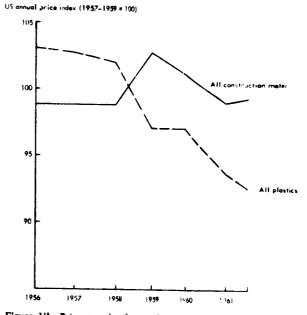


Figure VI. Price trends of general construction materials compared with those of plastics from 1956 onwards

4. The gradual growth of craftsmanship and specially trained staff without which plastics would not have shown the spectacular growth we have just discussed.

# INHERENT PROPERTIES OF THERMOPLASTICS

It is well known that the ability of thermoplastics to become a viscous liquid at high temperatures and to regain their initial properties upon cooling has resulted in a wide variety of techniques for converting the starting material directly into the desired product with the minimum loss of material and minimum handling. The properties of the base material are also reflected in the final product, often resulting in a definite improvement upon similar products made from traditional materials, or in entirely new applications for which previously no solutions existed. The more important applications, which have significantly contributed to the large tonnages mentioned earlier and have materially influenced the standard of living, will be briefly mentioned.

In the sphere of consumer articles, the production of injection moulded household goods should be mentioned, where plastic wash-basins, buckets, kitchenware and tableware have largely replaced the older galvaniard or enamelled iron products. Easy cleanability, resistance to corrosion and micro-organisms, coupled with mechanical strength and light weight have been the main factors responsible for this change. Developments in plastics film have led to entirely new packaging applications such as heavy duty bags for fertilizers which can be left in the open for prolonged periods, thus aboviating the need for storage space. Plastics film has also proved very successful in providing efficient, inexpensive and hygionis packaging for feedstufh, milk and pharmacoustical products.



Figure VII: Influence plastic structure serving as greenhouse

Speaking of packaging, the blown plastic container in sizes varying from a few cubic centimetres to 200 litres should not be forgotten. Milk, edible oil and detergents are only a few commodities packed in plastics in much safer and more efficient ways than with traditional materials.

There are, or course, many other interesting examples of plantics applications in the consumer article sphere which cannot be dealt with in this brief survey, but it would be a mistake not to mention plastic footwear. Here, plasticized PVC has made considerable progress, mainly because of its excellent wear resistance coupled with good weathering properties.

Plastics have also made great strides forward in the area of capital gouds, and first of all the success of plastic piping should be mentioned. Plastic pipe, usually based on polyvinyl chloride or polyethylone, is extensively used for water supply, both for domestic purposes and farmland irrightion. Plastic pipe compositions have been developed for drainage purposes and it is also possible to use adequately designed glassifibre-reinforced pipes for vervice at considerable pressures and resistant to aggressive chemicals.

Under the same category fail various agricultural applications of plastics, such as black film of excellent wouthering, mointure and microbiological resistance, which can be used to increase crops significantly by water retention and suppression of wood growth. Plastic groonhouses of varying design are being used increasingly and here mention should be made of the relatively new development of influted structures providing economical, regardly incided storage, factory or workshop spice (figure VII).

Finally, the inherent properties of plastes will lead to their increasing usage in the building industry. This will eventually lead to a reduction of building and/or maintenance arets and allow more rapid construction. Building with profetericated, light-weight panels, for instance, is already borosteing more videopread. Such plastic-based panels, have weather resistance and spuctanesis strongth, while by the use of feamed plastice encogetional heat insulation can be achieved. Figure VIII shows panets consisting of an outer skin of PVC and a core of polyurethane foam, while figure IX represents a building constructed with such panels.

All this does not mean that plastics will entirely replace traditional materials. More likely, the use of plastics in the field of building will be based on technicality and economically justified combinations with the traditional materials such as concrete, steel or wood, which in this way will be efficiently protected or reinforced. On the other hand, such combinations, e.g. by the use of light-weight components, may very well result in economies in the amounts of traditional material required.

#### PRODUCT AND APPLICATION DEVELOPMENT

The plastics applications mentioned in the proceeding paragraph illustrate the use of a particular set of properties of a particular plastic, but these properties are in all cases very different from those of the thermoplastic in the early stages of development. In time, a number of conflicting requirements will have to be met, highest mechanical strength, for instance, usually requires increasing molecular weight, but the ease of processing in an extrusion or injection moulding machine then becomes more difficult Similarly, flexibility can often be considerably improved, but at some sacrifice of heat stability. Each application, therefore, confronts the plastics processor whether he munufactures film, bottles or pipe, with the problem of selecting the right starting material. A considerable amount of work on product improvement and development has been and is still being carried out on the part of the plastic raw material producers to obtain

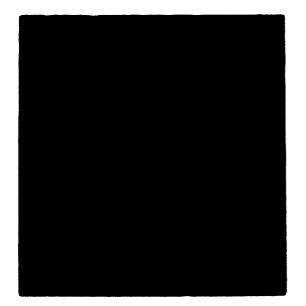


Figure VIII PV( four sandwish panels being ans rebind in a seed

modified grades more suitable for the application envisaged. This means that not only the number of different plastics increases, but every type of plastic now comes in a wide variety of grades carefully designed to give the best combination of both processing and end-use properties. As a consequence, every raw material producer has now available a variety of particle size, molecular weight, molecular weight distribution, type and amount of additives such as antioxidants, antistatics or flow improvers, in order to meet the most exacting demands from both the plastics fabricator and the end-user

These results reflect very much the efforts made in the research and development laboratories set up by the large plastics producing industries, who were anxious to build up the outlet of plastics as rapidly as possible By the very nature of the plastics raw material manufacture, acceptable costs are only to be obtained by largescale production units, and consequently a rapid build-up of the market during and after plant construction is essential it goes without saying that the cost of the research and development efforts involved in the product and application studies montioned, has also been enormous it is not possible to develop a grade of plastic for a given application without first building up a considerable know-how of the application concerned information regarding the requirements of the envisaged processing equipment and the demands of the plastics fabricator and the end-user is likewise essential, as is a detailed knowledge of the ultimate conditions under which the article will be used Finally, it is not enough to have all this information regarding the requirements, it is also necessary to know how to most them by adjusting the many variables in the plastics manufacturing process in order to obtain the right product

In the course of these activities, the large plastics manufacturers have not only developed special grades for specific purposes, but also entirely new ideas for



Pipers III. Patient building conserving to day construction down in dama VID

plastics applications have been worked out, some of which have been previously mentioned. In this way manufacturers have amassed tremendous experience in practically all fields of application and they have not failed to use this experience in concentrated efforts to provide technical assistance to their customers, who were thus freed from many problems the solution of which would have been very costly and time-consuming to them. Customers could, therefore, concentrate on the technical and commercial aspects of plastics fabrication riself, and could thus make a much faster start than otherwise would have been possible

Nevertheless, because of the enormous work involved. the product and application development efforts have taken much time, and this explains the sometimes considerable time-lag between the first recognition of the potential scope of a plastic and the start of large-scale production. It is felt that the necessity for this type of work has to some extent determined the rate of progress of the plastics industry in the industrialised countries. Developing countries, it is felt, are in this respect now better off than the industrialized areas in their early years of plastics developments. With the results now available and the know-how being freely passed on, together with the plastics, by the manufacturing industry to its customers, one potential source of delay has been eliminated or at least greatly reduced, and a faster growth rate should be possible

#### DEVELOPMENTS IN PROCEEDING MACHINERY

After thus having briefly reviewed a number of the main applications of plastics, it is appropriate to emphasure that the achievements mentioned would not have materialized but for the considerable development effort on the part of the manufacturors of plastics processing equipment. Although the principle of injection moulding was borrowed from the light metal industry, far-reaching aborations proved necessary, and entirely new principles of machine dosian and construction had to be worked out Move particularly, the specific properties of plastics in the motion state had to be taken into secount in order to arrive at machine designs giving optimal results, from the point of view both of quality and of production speed the quality of the finished article depends not only on the planetic base material, but also to a large extent on the degree to which the machine manufacturer has been able to adapt dougs, pressure and temperature gradients. surew and mould construction etc., to the molt and solidfunction characteristics of the plactic to be processed All shoes factors determining the quality of the finished artsole have been and are still being studied in a print effort by machine manufacturers, mechanical engineers. separates and technicians to elusidate the basic phonomenu taking place in the various "unit operations" of plasters processing. The understanding of these phenomena has poned many new processing routes for plantics

Normadaya a refused range of manhates and territs metter for reportion moulding, blow moulding, compression moulding, film blowing, casting, cheetohing, calendering, pasto processing, comproveding, cheet entrusion, pipe metrusion, from production etc., and any or improved



Figure X. Extrusion of 10" PVC pipes for service in water-supply systems

techniques for plastics processing are still being discovered. leading to new approaches in plastics engineering. Important improvements have been made, e.g. in equipment for injection moulding and extrusion. For injection moulding not only considerably larger machines have been constructed, but also the basic technique has been improved by the introduction of preplasticizing units, screw operation and automatic control. In extrusion operations likewise, a wide variety of principles and machines has been developed. To quore a few examples

(a) Extrusion of rigid PVC, previously rather critical in view of the decomposition of the polymer, no longer presents serious problems, and figure X presents a pipe extruder operating at high levels of speed and reliability which only a few years ago were considered unattainable

(b) Strong, clear film with excellent mechanical properties, making full use of the intrinsic properties of the plastics, can now be made at ever-increasing speed.

(c) Bottle blowing can nowedays be done on an industrial scale with most of the general purpose thermoplastics. Production rates of 4,800 one-litre bottles/hour are already considered quite normal, and figure XI illustrates a machine capable of such production rates.

Thus, processing machines are becoming more and more reliable and versatile, and it is fair to say that much of the dolay between the early concepts of plastics processing and the present growth of the plastic industry was partly due to the absence of adoquate equipment. and machine manufacturers, both in the United States and in Europe, have by their constant efforts consider ably contributed to the bridging of this gap between conception and realization. Table 1 attempts to Hustrate is, hoting the major machine developments since 1935 Here again, what may have been a limitation in the past has now been completely overcome and industrializing countries are now confronted with such a large assertment of plastics processing machinery that the problem has some one of selecting the right equipment for the job in hand, rother than of matching materials, products and projects to concentially madequate machinery. Anot n should, however, be over idered, vie that of ne well-trained personnel to operate the reli

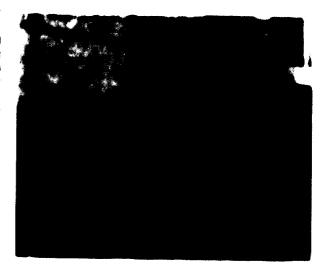
TABLE 1. SURVEY OF MAJOR DEVELOPMENTS IN THE PROCESSING OF PLASTICS SINCE THE RINE OF THE PLASTICS INDUSTRY

injection moulding	1915
Calandoring Before	
Extrusion Defore	
Automatic injection moulding	1917
Biaxial film stretching	1945
Now moulding	1946
Film extrusion	1946
Injection moulding with preplastigation	1946
Vacuum forming	1946
Whirl sintering	1952
Screw injection moulding	1953
Flame spraying	
Moulding by powder sintering	1956
High speed automatic blow moulding with parsion control	
or ram accumulator	1966)
New assisted vacuum forming	1760

yet often complicated equipment, to maintain the machinery and to plan and supervise the operations.

# TRAINING AND TREMNICAL EDUCATION

The rise of an ontirely new industry, such as the plastics processing industry undoubtedly is, requires special personnel and necessitates special training and education. The plastics processor will require staff with knowledge and experience of the new materials new available, and of their properties and processing behaviour. He will require staff with knowledge of the processing equipment and capable of using this equipment and maintaining it in working condition. The plastics industry will further need craftemen who can work with plastic intermediate products like sheet or pipe, who know how to wold, cut and shape the new products and in general, at various supervisory levels staff will be needed whe can direct



rigere 36. Adaders bette blendag machine, agedite of making 4,000 /-Bre basilies per hour

TABLE 2. VARIOUS EUROPEAN INDITIUTES INGAGED IN PREMITIONAL ACTIVITIES IN SUPPORT OF THE PLAFFICS INDUSTRY

Country	Mathiet.	Ever of organisation	<b>Noam</b> responsibilistes or functions
Unter! Kingdom	Plantics Institute	Assessation of prominent experts	To dolline aducation requirements and programme Co-ordination of various adjacational activities
	RAPRA	Gevornment muliture	Promotion of interests of the plastse industry, experimental contract work and information service
	j Yaroloy Research Laboratories Ltd. (Chessington)	Private	Contract work for the industry
	Arthur D. Little Research Institute (Inversel.)	Private	Contract work for the industry
Prenes	Concervatoire national des arts et matiers (Paris)		Education in plastics technology at acade mic level (ingeniour)
	Boole nationale des mattères plasti- ques (Oyonnan)	Gevernment	Education in plantics technology at inter mediate level (technicten)
	Collige d'enseignement technique (Connevilliere)	Gevernment	Education in plantics technology at inter mediate level (technicien)
	Contro d'étudos des matsères plan- tiques	Gevernment/private	Contract work for the industry
Pederel Republic of Commany	Arbeitagemeinschaft Deutsche Kunststoffindustrie	Private association	General promotional activities are in commution with technical education Quality control and specifications
	Bundssanstalt för Muterialpröfung (Burlin)	Government ministure	Contract work for the industry on process ing and losting of plastos
	Materialpröfungsumt Nord Rhom-	Geverament mutitute	Contract work for the industry on process ing and issuing of plantics
	Bassalla Institut Prankfurt/M	Private rossarch organization	Contract work on all aspects of pluster polymorustion and technology
	Barmatadt and Aashan Universities	Gevernment	Educational responsibilities for plastic (seguther with 10 other universities) a academic level Contract work for the industry
	II Stantliche Ingenieur-Behulen	Cievernment	Educational responsibility at intermediate technical level
	Carl-Duisborg Goarlischaft	Gevenninget	F2-month course on plastics processing of the seape of the foreign assistance programme
Mathematic	. Kunststoffen kustikuut TN.O. Dolft 2	Gewenstedt	Independent research on plastics propose Contrast work for the industry Conserv information and promotional activities Lasteries and training courses at various
	Caserial Laboratorius 7 N.O.	G	technical levels Among many other projects, independent fundamental research on plastics is a carried out

the over-all activities, design the activities, plan the programmer, in short, "think" in plantics.

# (a) Professional and

The requirements of the photon pressuring solution, as for a solution pressure on conserved, will depend on the production programmer. In general one could say that pressured with the following lowly of solutions observes will be model

University graduates with special photons reasing and background of mechanical expressing, chemistry or physics. Universities in most of the industry, hard counries have recognized this could next of them new have an or more expected between a photon and data ofter appartunities for experimental study. It is believed that in this respect the Fodoral Republic of Cormany to-day is the most advanced country

#### (b) Plastics ingineers

In this category plastic processing experts are required with a general knowledge of plastics and experience in a versity of machines, in mould design and construction and in maintenance of equipment. Here, tao, in the industrialized countries the required education is new gradually being provided.

# (c) Plane Joremon

Plant foromen have, in the past, mostly been resruited from the motal industry after proper training, but provisions for this type of education are now being made in France for instance there are two special schools offering 3-year courses directed at three types of work machine supervision and maintenance, actual processing of plastic and production of glassifiere-reinforced articles

#### (d) ( raftaman

Craftsmon with experience to work with intermediate plastic products like sheet or pipe. Requirements are a general knowledge of plastics, and experience in welding, jointing, adhesives, thermoforming etc. Trade schools are new gradually incorporating this type of traising in their programmes.

It is believed that the lack of sponsally trained personnel has to some entent restricted the growth rate of the plastics industry, particularly in the earlier period. Although in various countries the need for more spootle technical training had been recognized already long before the war, and various measures were taken, results were rather elew to appear, memby because of the difficulty of finding training staff. The situation in various industrialraid countries has new much improved, but there is cell a considerable shortage of well-trained plastics technolegists, supervisors and operators, which is full by the industry, who have therefore attempted to organise educational schemes themselves.

One way of doing the has been by promoting the creation of "Plastics Institutes" that have arranged ocuraes, between, hold enaminations and efford arranged sources, between, hold enaminations and efford arrange. As an enample the "Plastics Institute" is the United Eingdom should be stantioned, which is a professional organization of exports promotion in the British plastics industry. This Institute has, is on-operation with aniversition, technical orbicals etc., formulated requirements for technical education and established diplocage at various levels.

Back activities are constitutes combined with a laboratary function to provide the processing industry with independent advice and to carry out standardination work conserved with test methods and material quofunctions. This is pertorderly true for processing of anti-procession institutes, each as the Plastes business 7100 is the Nucleorlands, which also only quotid problems accountered in the industry. The table on page 500 process a survey of each activities, their scale companyibilities and the way in which they have been financed and organused It is felt that any country wishing to promote its plastics industry will be involved in educational problems rolating to the provision of skilled sechnical personnel and that there may be an advantage in hoing able to take plastics training into account when considering tachnical aducation at large, rather than having to squeeze it into already existing and sometimes not so flexible systems of aducation. Nevertheless, the availability of whiled craftement engineers and professional staff in other branches of industry, who could in relatively short periods he given training and background in the field of plastics technology has definitely helped to bridge the rather long period when official plastics education in the industrialized areas was lacking. This possibility dues not exist to the same extent for the developing countries, where it will be necessary not only to provide personnel in the plastics industry itself, but also training stall for those personnel. Taking into account the onperionce in the industrialized areas, it is suggested that the attempt should be made to setablish both categories multaneously, making use of the educational possibilities now available in the industrialized countries. In this vonuestion the month might be considered of establishing a Plastos institute, that could work out plans, investigate industry staff requirements, advice on educational motions, organize training courses and serve as an advivery centre for the emerging plastics processing industry In this way the new industry would obtain in addition to the service and support they will obtain from the raw material producers independent information regarding equipment, prices, quality, etc. Consideration could. perhaps, he given to the setting up of such an institute jointly for a group of countries, which would simplify stalling problems and avoid duplication of effort

It can be assumed that both raw material producers and manufacturers of processing equipment would volcome such developments and would be happy to contribute by putting their experiences and hapw-how of the plastics industry wirele-heartedly at the dispusal of such institutes.

# Concil verser

Prom the preceding partgraphs a sumber of constantions result that might warrant further consideration

- Program in plastics in the industrialized countries effloringly impressive. Less in the part basis delayed meanly by the undustliarity of the products and proremes, the time-concursing procedure of improving plastics quality, the back of adequate processing equipment and the relativity dow program in technical effortune.
- 2 Annung the vertices applications of plantins there are many that constraints instantially to the standard of living other directly as conserver guests or indirectly is the form of applications are if importants, reside a planting applications for vertice applications for section, is a company to be a form to be a strong one for action, is a companying direction to be a strong one for action, is a companying direction to be a strong one for action. Here hereas, plan, thus, one.

3. For a longe complex of weddy different, conservingly important applications. Fully adopted types and grades of plastics over and reliable processing optigatest is predictly. Forkness support from plastics predictors and marking manufacturers is blowns ornitable and thus many of the limiting factors of the part laws been diminized. A regist growth of the plastics processing industry is developing econtriles may, therefore, is expected.

the character is a large state of the second s

4. Technical education in commection with plastics will be a point of concern, but the educational systems now in use in the industrialized countries and designed to most the domand for plastics exports offer the possibility of a relatively fast start. Establishing Plasties Institutes might be considered as a means of defining the needs of the plastics industry with regard to personnel, of contributing to or preparing training courses, and of serving the industry with independent advice on technical or commencie matters.

# 10. PLASTICS AS CONSTRUCTION MATERIALS FOR DEVELOPING COUNTRIES

Arthur P. Lion, Buttollo Momorial Institute, 1 USA

# PART 1. CURRENT TECHNOLOGY AND ESTABLISHED APPLICATIONS IN MATURE ECONOMIES

# INTRODUCTION

Polymers and plastics constitute one of the fastest-growing and most versatile members of the petrochemical family. In both the United States and Western Europe, construction applications comprise one of the largest single uses for these materials. Before attempting to assess the possibilities for exploitation of plastics to meet the construction needs of developing countries it is necessary, therefore, to review the state of the art in thene advanced economies.

Although much progress has been made in building applications of plastics, a number of companies in the advanced countries are continuing to spend huge sums on further development. One needs only to follow the trade journals to realize that predictions of a short time and have become established fact and that technical development is in an extremely active state indeed, the housing industry in the United States and Europe may be said to be at a point not only of rapid evolution, but, in many respects, in a stage of revolution. This attempt, therefore, to review the present state of development must be taken as morely illustrative of solid accomplishmonts, with omissions of many cases that might have been used. Discussion of new trends and projections likewise will also be merely illustrative, for we are learning more intelligent applications of plastics day by day. The objective of this part of the paper is to establish a base on which to build, in projecting where and how the needs of developing countries may be included in the current evolution-revolution of building construction involving plastics.

# MAJOR PLASTIC TYPES USED IN CONSTRUCTION --COMPARISON OF PROPERTIES

The types of plastics finding major use in construction are listed in appendix 1, table A-1, along with pertinent property characteristics. These plastics types fall into two major classifications : thermoplastics and thermosets. The thermoplastics can be formed and reformed by heat and pressure; they have only secondary attractions between molecular chains, and these attractions can be weakened by heat. Thermosets, on the other hand, have a high degree of primary linking or cross-linking between chains and are essentially inconstitive to temperature. Comparative characteristics of representatives of the two types of major materials as they relate to construction applications may be briefly illustrated as follows.

#### Thermoplantics

Of the more common thermoplastics, polyvinyl chloride (PVC) and acrylonitrile-butadiene-styrene (ABS) have been most actively investigated for structural use. Available as an unmodified polymer, PVC may be compounded with stabilizers, lubricants, and pigments. Modified PVC contains up to fifteen parts of one of a number of rubber or rubber-like polymers. Improved processing techniques have made it possible to fabricate parts from the latter type by both injection moulding and by extrusion.<sup>9</sup>(1) Lower cost is the major factor favouring this development.

The ABS plastics have some advantages over PVC, but in general are somewhat inferior to PVC—for example, in long-term strength. The strength of ABSbased plastic material is proportional to and largely a function of acrylonitrile content. The amount of acrylonitrile present is also reflected in increased cost. The ABS plastics have a lower specific gravity than PVC (1.05 to 1.06 *versus* about 1.35 to 1.40 for the latter) but the cost/lb as well as strength characteristics provide economics favouring the PVC. However, processing of the ABS plastic is generally simpler, particularly in injection moulding. Thus, ABS plastics are finding greater use in moulded parts while PVC is being used for extruded sections in ever-increasing quantities.

Polyolefins, such as polyethylene and polypropylene, are finding increasing use in construction. Although some of the polyolefins have significant limitations with regard to structural applications, polypropylene and high-density polyethylene have a sufficiently high modulus (rigidity) to be considered for a number of structural uses.

# Thermosets

The general class of thermosets includes such materials as phenolformaldehyde resins, epoxies, melamines, and polyesters. Fibre-glass reinforced thermosetting plastics

<sup>&</sup>lt;sup>1</sup> Substantial contributions were made to this paper by the following members of the staff of Battelle Memorial Institute : Joseph E. Buruh, Charles W. Cooper, John R. Hagley, Richard T. Lasko, and Granville H. Sewell.

<sup>\*</sup> See bibliography, page 41 (part 2).

(FRP) represent the highest strength materials Appendix I table A.2, describes the common strength parameters for typical products of this type in comparison with other plastic materials. The strength of the FRP materials is due largely to the type and amount of the reinforcement As is the ane with any composite system there are many ways , which the components on he introduced and oriented.

The FRP materials can be assembled in highly misoiropic (proforentially orientated) arrangement to obtain the greatest benefit from the highest strength componentjust as is true in the case of reinforced concrete. In general plastics provide a higher degree of latitude than concrete in the choice and arrangement of reinforcing materials in developing countries, the pensibility exists of using materials other than libre glass for reinforcing or filling plastics. For instance, many cellulose waste products such as graded sugarcane stalks, or other fibrous materials could both reinforce plastics and minimize the quantity necessary for some applications. Further research effort will be required, however to develop satisfactory products from these low-gride materials because of problems of water resistance as well as fabrication.

# CONSTRUCTION PRACTICES ROLE OF PROPERTIES OF PLASTICS

#### Methods of fabrication

In general, where parts have a uniform cross-section or can be made from such sections, extrusion methods (2) are used to produce the part. When complex shapes are involved, injection or compression moulding is used. When parts are fabricated from more than one type of product, casting, compression moulding, and mechanical assembly are frequently involved.

The fabrication of composite structures frequently employs other materials in conjunction with plastics. Fibre-glass reinforced plastics, laminates of paper. glass, wood fibres, steel, foam, honeycomb shapes are all part of the over-all group of composites in which plastics can and do play a dominant role. The role of plastics in composites is usually associated with their ability to bond other materials into a functional structure. They may be used as adhesives to bond wood, metal, paper and glass together - either in sheets or as the binder in castings. These systems can be homogeneous, as in laminated beams or castings, or they can be constructed in such a manner as to place high-strength components at the point of greatest stress. The latter application is exemplified by wall panels and doors, where the skins have the high strength and the core may be foam, honeycomb, or other low-density materials which depend on the composite structure for strength.

# General advantages and limitations in construction

The more conventional materials of construction which have been in use for many years have many limitations which have been recognized and accepted. Iron and steel, for example, are subject to corrosion by the elements, with subsequent weakening. Wood loses strength on aging through deterioration attack by various organisms or even by a change in its mosture content. Without protection from the weather most words will degrade capidly. Even concrete is subject to spatling, and fur thermore without reinforcement, is structural strength except in compression is very low. Ceramic or glass like materials offer the best resistance to weather and other natural causes of degradation, but relacively small sections of such products must be joined by means of cement, organic or morganic, and these latter materials represent a valuerable area.

Similarly plastics have eitam limitations, but many of these can be either compensated for or concented by compounding conforcement or proper choice of product. Certain thermoplastics are designed for service below the freezing point and above the boiling point of water. As a class, thermoplastics will generally perform satisfactorily (broughout a temperature range of about 40 to 140° F (3) The thermosets, as previously mentioned retain most of their strength at much higher temperatures Although ultraviolet (ght is an inemy of virtually all polymeric materials, some to a greater extent than others this is not a serious problem, for the addition of 1. V screening" agents or pigmentation greatly improves light resistance. Furthermore most fabricated products. such as pipe are generally used inside structures or are buried in the wolf, where light is not a factor

Although most plastics can be abraded by agents such as wind-driven sand, metals and wood, as well as glass, they are also subject to damage by this means. Often the selection of the product will alleviate much of this difficulty or, in other cases, the effect of abrasion can be greatly reduced by compounding with an elastomeric polymer, as in the case of PVC

According to recent statistics, and contrary to some reports, plastics are not more hazardous than other materials with respect to contributing fuel to feed a fire. The US National Bureau of Standards data showing Btu's per pound are Paint films 3,500-6,500, unpigmented varnish 12,000-15,000, wood 6,500-8,500, cork 11,000; plastics as low as 100. On rate of flame spread, where cement asbestos board is assigned zero and red oak flooring 100, PVC and fire-retardant polyester are rated at 20 to 35. Smoke can also be a very serious hazard, but the relative hazards of smoke and fiame have vet to be rigorously defined. Even though some plastics are superior and most plastics compare favourably with other organic materials of construction, further work is desirable on fiameproofing as well as on the development of a wider range of flame-resistant and non-smoking plastics.

With the exception of certain polyamides and some cellulose derivatives, plastics are virtually unaffected by moisture or water. In fact the polyolefins, polymers and copolymers of vinyl chloride, many of the polyesters, and a variety of other plastics are extremely good barriers for moisture, and some are in common use in water systems. With respect to corrosion resistance, virtually all plastics are superior to common metals. Most plastics are immune to microbiological attack. Although a few materials may contain plasticizers which offer some source of nutrient to micro-organisms as well as insects, the degree of unsupplicity in extremely low compared to that of wood and other cellulous products. The proper velocition of materials for a specific and use will eliminate mont difficulties of this nature

Research presently going on is designed to create materials with greater environmental resistance A conlinuing programme of this type will help to meet specific problems as they arme. I has far there has been no serious without in the resputity growing use of plantics in construction and other fields because of luck of environmental resistance. The emergence of new products and the modifiuntion of alder ones has more than kept pace with struc tural and environmental domands (4, 5) The wide accomtence of plastics by military and space agencies supports this view. In fact, research for these agencies has helped to broaden the horizon for these synthetic polymers.

# Strength and structural factors

Comparisons of reinforced plastic materials with wructural metals are not unfavourable to plantics when one considers key factors actual strengths of fibre-glass reinforced materials in many area approach the yield of mild steel and aluminium alloys, the strength-toweight ratio is highly favourable to plastic materials the low density of plastics is advantageous not only in reduc ing structure weight, but also in simplifying transportation, relative ease of fabrication, particularly with regard to complex shapes, is a distinct advantage in the case of plastics, excellent resistance to corrosion is one of the important factors. While price comparisons do not in all cases favour plantic materials, particularly in the case of reinforced systems, cost calculations frequently presuppose a nearby raw material source. In many areas of the world this may work to the advantage of plastics, particularly in many of the developing nations where petroleum is in abundant supply and metallic ores are not.

FAMLE F. HARVERTANT PROPERTIES OF TREASTORNESS PLANTES

Marrisenni factori	Economic Auctors
lansile strongth	Croop (cold flow)
Compressive strength	Streets rotanation
Flexuret vtrength	Apparant modulus
Impact strength	Strong-risplane (sme iconstant icaci)
	Patigue strongth (cyche loud)
	Aging characteristics

the strength properties of plantics can be divided into whore and long-term factors. Both are important, but long-torm proportion are the most critical in most applications. Table | lists some significant proportion, such as croop, long-term strongth (rupture strongth) modulus, and agong officets, for both types. All plastics and partscularly thermoplastic materials, show decreasing wrength with time of application of the load and with increasing temperature. The stress-rupture time curves at ambient temperatures follow the same general pattern as metals at elevated temperatures

# PRESENT MAJOR USES OF PLASTICS IN BUILDING

Although plastics have been available to the construction industry since the early part of this century, not until recently have they been used for any but the most minor applications in building construction. As with any new materials, plastics were not accepted readily initially, in many cases, they were used as substitutes for other materials or they gained a reputation as a "cheap" or inferior material. Overcoming these psychological handicaps has not been easy. However, because of their

TABLE 2	PRODUCTION OF	PLASTICS IN	THE UNITED	STATES -	1960	THROUGH	1962	
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		Total produce	M		Construction applications							
		(million pound			Million pound	•	Per cant of total					
	1960 •	196/ •	<b>1962</b> b	1960 •	1961.5	1962 h	1966 -	1961 *	1962 ·			
Acrylics	145	150	170	29	37	43	20	~				
Alkyd Resins	367	499	524	230	294	296	63	26	25			
Cellulosice	143	148	158		3			59	56			
Coumarone-indens and Petroleum			1.74	5	3	2	2	2	1			
polymers	232	281	325	178	140	1.80						
Epoxies	63	70	82	1/0	169	172	77	59	53			
Melamine and urea	368	446		1	1	3	2	2	- 4			
	543		497	111	112	121	. 30	25	24			
		665	693	184	197	214	- 34	30	31			
	157	193	217	23	28	31	15	15	14			
Polyethylene	1,336	1,606	2,016	147	170	196	11	11	10			
Polypropylene	41	97	144	0	0	0	0	0	Ö			
Rosin modifications	128	120	135	20	23	25	16	19	19			
tyrenes	974	1,145	1,268	167	191	189	17	17	15			
/inyla	1,167	1,260	1,360	305	355	448	26	28	33			
Miscellaneous	145	181	214	2	1	7	1	0.5	33			
TOTAL	5,768	6,861	7,803	1,400	1,581	1,747	24	25	22			

\* Chamical Work, 91 (4) ; 53 (1962).

\* Chemical Week, 93 (8) : 81 (1963).

versatility and adaptability to general construction practices, as developed in the previous section plantics have grown out of the inferior stage and are now accepted as a quality product in many building applications ranging from the foundation to the roof.

# Total volumes by type

The growing acceptance is reflected in market volume as shown quantitatively by the figures in table 2. The amount used in building applications went from 1.40 bit item No in 1960 to 1.75 billion. No in 1962, or a rate of increase of about 10 per sent per year. Bused on total production, however, the percentage going into construction has remained in the area of 22 to 25 per cent.

It is understand, though not documented, that plastic construction products in Weistern Europe have been more widely scoepted and that the percentage of total plastic production going into the building industry is higher than in the United States. Futimates of this percentage range from 25 per cent upward. Table Undentifies plastic production for Western Europe for a variety of plastics in 1961. Total production is very near or equal to that of the United States. On the basis of the abovementioned percentages, on the order of 2 billion the of plastics are going into building products each year in Western Europe.

# Volumes used in major applications

**Based on the same data as shown in table 2**, the brunkdown in table 4 shows major areas of application of use of plastics in building. The following paragraphs touch on significant aspects of these well-established and growing uses.

# Surface coatings

The major single use for plastics listed in table 4 fails in the category of coatings and paints. In the post-war period, several synthetic-based materials, such as alkyds and latices, started a trend away from the more conventional oil paints, lacquers, varnishes, and enamels. Such plastics as urethanes, acrylics, polyesters, epoxies, and vinyls are demonstrating better qualities of toughness and durability, ease of application, coating tightness, and wide versatility than other types of available coatings.

TABLE 3. WEBTERN EUROPEAN PLASTIC PRODUCTION IN 1961 \*

	 	 	 	 	 	Volume (million lb)	Per com of total
Polyo <b>lefins</b> .						730	11.7
Vinyls						1,830	29.2
Styrenes						680	10.9
Phenolics .						760	12.2
Aminoplastic						760	12.2
Alkyds						600	9.6
Others						890	14.2
						6,250	100.0

+ Chemical Week, 92 (19): 53 (1962).

FARES 4. MEASUR CORE OF APPENDIX IN MULTI STREE APPENDIX ALLENDES. E. MERCE STREES, CORES

- And the standard of the standard stand Standard standard st Standard standard Standard standard Standard standard Standard standard Standard standard Standard standard Standard standard Standard standard standard stan	
l pphi a cen	i dum nathun b
( meings puints	
ff texering	<b>41</b> .2
Wire contings	1484
Composite panels, physical and hardhoard)	151
Monstare harries and insulation	1.563
Papatri	**
Phanta particis	14
Lighting fixtures	4.4
We all sile	17
A Supragraphic lighterioides	12
Fixture both plumbing	14
( )ther	14
	1 147

( hemical Week 93 (8) 83 (1963)

The urethane coatings are available in a number of formulations and can be used as either a clear or a pigmented finish and applied by brush, spray or other conventional applicators U-rethanes have good durability over interior wood floors in glue laminated beams as a clear varnish on exterior wood siding where the ability to resist wear, chemical, and sunlight action is an essential attribute and for specific wood categories such as cedar cypress, and redwood which up to now have been hard to maintain because of their oil content. In addition, urethanes have been used to seal concrete floors and exterior concrete wall surfaces.

Polyester coatings, which have been valuable in furniture finishing, have been used by one manufacturer of prefabricated houses as a protective coating for exteriors. Attention has been given recently to the use of acrylics in coating wood and aluminum.

Epoxies provide very good adhesion, hardness, and resistance to weather, chemicals, and acids. Since these coatings do not shrink as they harden, they can be used for patching old concrete or other masonry surfaces and can be finished to a feather edge. As a result, these coatings make possible resurfacing of entire concrete floors with a coating thickness of less than 1/4 inch.

Vinyl coating formulations have been especially good for weather-proofing and sealing preformed reinforced concrete structures and folded plywood roof forma. Although some problems have developed because internal vapour pressures were not released through the coating, these are being lessened by the use of special insulation and by special formulations.

# Plastic pipe

Perhaps the most dramatic growth story is that of plastic pipe. The 1963 figures in millions of pounds are as follow: (7)

Polyethylene													56.6
Polystyrene .													
<b>PVC</b>		•	•			•	•	•			•		19.1
ABS	•			•					•	•	•	•	12.5

Despite an increase in annual dollar volume of approximately 12,000 per cens over the pairt 15 years, the market for plantic pipe could increase another 100 per cens over the present volume in the next 10 years (8)

An increasingly significant factor in this growth picture is cont. Detailed data for plantic and metal pipe are shown in appendix 1 table A 3 and are summarized in table 5 to illustrate significant cost comparisons. In addition to savings on materials in a number of cases light weight facilitates handling, and ease of cutting and joining (solvent weight) saves labour costs. The availability of polyethylone pipe in king lengths is undoubledly one of the reasons for its growing use for water and gas piping.

Also of importance in accounting for the dramatic growth in volume of plastic pine is the intensive effort on testing and setting improved standards by the industry in both the United States and Europe. As a result plastic pipe has become more and more acceptable to building code officials and architects for phumbing uses. With increasing understanding on the part of building code officials, plumbing codes are being changed to include the use of plastic pipe and littings. For example, the Federal Housing Administration of the United States Government, which guerantees many leans for new houses in the USA, has accepted polyethylene for exterior water lines, several types of plastic for sewer lines, and A BB for drain, waste, and vent. Polyvinyl chloride drainage pipe is also being used in Europe and 'apan and is considered as standard piping for drainage, sewer lines. water mains, and cold-water service lines in these areas, PVC prossure pipe is being used in Europe for coldwater servicing lines in housing, but is generally not used for hot-water service because of inadequate heat resistance.

In Denmark, polyvinyl chloride pipe, ranging in sizes from 1 in. to 14 in., (9) is available for water mains, sewage, and irrigation. In the Federal Republic of Germany, polyvinyl chloride is being used in laboratory and household plumbing. German building standards require water pipes to withstand pressures to 102.2 lbs per inch. Dynamite-Nobel A/G is now successfully producing PVC pipes capable of withstanding ten times (9) these requirements.

#### Insulation

The thermal conductivity of most plastics is unsqualy low. Formul plastics such as rigid wothane, with a "K" factor of 0.13 and polystyrene with a factor of 0.24. are superior to "natural" insulation materials such as cork (K = 0.19) and mineral wool (K = 0.27). Polystyrene heard receiving major attention in relation to other formed plantic materials currently lends all of the formed plastics in architectural applications.

In the evolutionary process of converting to plastic materials, it is probable that the gratest immediate prioritial for foams apport to be in sandwich panels. However, since foams have a minimum directional deformation in relation to other plastics, they are capable of carrying structural loads created by wind and snow Consequently an efficient use for them would be in the structural frames of buildings a use stready domanutrated in principle by the construction of rademos for Distant Early Warning Systems in Canada

#### Reinforced sheets

Translucent or opaque, plain, and corrugated reinforced thermoplastic shoets are also being used more and more for exterior and interior walls, partitions, roofs, and skylights. These shoets are widely used in Western Europe ind Jupan for shop fronts, office buildings, and industrial ouildings. Some applications of this nature are being made in industrial buildings and office buildings in the United States, but early problems in colour retention have hindered the growth of this market. With additional effort on the part of the plastic producers to overcome this problem, better formulations have been established to prevent colour fading. A wide variety of new uses for reinforced fibre glass is emerging and will be discussed in a subsequent section.

# Other applications

One producer of prefabricated homes provides some of the answers to the question of where markets exist for plastics in building. This organization — which produces some 20,000 homes per year — uses injection moulded

TABLE 5. COST COMPARISON, PLASTIC VS. METAL PIPE \* (\$1 lineal foot----1964)

Nee	Capper	Gairanised steel	Can iron	Poly- ethylene	PVC 169	Schedul Jû
Interior supply						
1/2"	0.26	0.18		0.05	0.11	0.21
1″	0.62	0.33		0.15	0.17	0.43
2	1.72	0.72		0.60	0.45	1.00
Drain, waste, and vent						
2-1/2"	1.23	1.08		0.69	0.65	1.16
<b>4</b> <sup>•</sup>	2.55	2.16	1.50		1.60	2.97

\* Derived from appendix 1, table A-2.

• Schedule 40.

abinots, wholves drawers, PVC window multions polyntyrene foam-core aluminum doors polystyrene foam understab insulation marble dust reconstituted with polyaster for lavatory tops, and flexible 3 mil him for collings and walts (7).

There are many other areas in which plastics have been accepted and are being used as a quality product. They include

Awnings	formt lines
Caulting	Lighting punels
Counter tops	Monsture hurriers
Conduits	Mouldings
Curtain walls	Roof components
Door parts	Sandwich panels
Electrical insulation	Screens
Gas mains for pipe ribh	-
ings)	Water mains
Interior trim	Window sush

#### LIMITATIONS AND BARRIERS

With the growing popularity of plastics and so much obvious opportunity in construction, why has there not been greater use of it by the building trades? There are a number of general reasons and they don't always apply to each country or area in the same way. The major factors in developed countries, however, are tradition, unrealistic and restrictive building codes and regulations, technical and engineering obstacles, and costs.

# **Building codes and regulations**

A major obstacle to the acceptance of plastics in building is in the multiplicity of regulatory agencies. For example, a survey of 900 cities in the United States by the National Association of Home Builders shows that 71 per cent of the cities base their codes on one of the four proprietary regional codes. (10) The survey also indicates that almost all of the 900 cities have modified the model codes to their local liking. For example, over 90 per cent of the cities have adopted the National Electric Code, but 73 per cent have amended it to their situation. Because over half of the cities prohibit the use of prefabricated wall components, the regulatory systems of the United States are not only a barrier for plastics but they are also a barrier for many other new materials or products in the building industry. The reason for this - and herein lies the fundamental problem - is that most of the codes have been material codes. This means the code is basically written to approve certain materials and methods only, rather than specifying minimum performance as the guiding consideration. Fortunately, there appears to be a trend toward application of the uniform performance standards to which plastics as well as all other materials must adhere.

# Technical and engineering shortcomings

Before the chaotic situation on codes and regulations can be expected to improve, significantly more attention must be given to product standards and design criteria by the plastics industry itself. In the developed countries there has been a lack of understanding notionly in the part of those who approve that also by those who design, specify and use plastics. This includes a lack of uniformity in communication and a lack of understanding on such things as

- (1) Plastics terminology
- (2) Performance data related to both accelerated laboratory testing and actual installed performance
- (3) Extent of design capabilities of plastics

Failure of plastics as with traditional materials, is more often due to misapplication rather than to inherent failure of the products. The lack of uniform and meaning ful product and performance standards has been recognized by the plastics industry as a problem that must receive industry wide attention. Steps are being taken through its associations, engineering societies and by individual manufacturers, but a great deal remains to be done. The results of these efforts will be of tremendous value in developing countries to give plastics a running start in building applications.

Prices

The factor of cost to the consumer cannot be ignored, and, of course, will  $b^{+}a$  determining factor in rate of growth of plastics in developing liations. Until recently, many plastics were not competitive with other materials in building applications, advantages other than directly comparable prices have been largely responsible for their growth. Market prices, however, have continued to decline and a growing array of plastics are becoming competitive with conventional materials — in many cases, more economical. Specific examples will be given in a subsequent section.

#### Ties to tradition

The majority of current residential and non-residential construction in developed and developing countries is being built by methods that were developed over 100 years ago. The fact that the majority of our houses are built by erecting wood studs and then applying a series of lavers of materials attests to this. Many large commercial buildings are also still erected brick by brick. As a result, the construction industry is one of the very few that has not generally adopted new industrial methods. There are many reasons for this. Many new houses are constructed by the owners themselves. The general public has been very slow to accept new materials and methods of construction. Building commissioners have been reluctant to adopt new codes, let alone accept new materials and techniques. And, finally, labour unions have discouraged use of new materials as well as new equipment - especially if proprietary interests of a particular trade have been threatened.

The key limitation to the acceptance of plastics in the past has been the consumer or user. A basic similarity exists in the people of developed countries and developing countries in that the majority is bound to traditional materials and methods of construction. When these materials are changed, the consumer has little basis for evaluation. The individual wants a product that he knows will perform adequately and seldom wants to take a chance, even though the manufacturer may have spent a fortune in research and testing of material. At the same time, there is generally a strong impulse on the part of individuals or families to maintain the same material standards existing in the immediate neighbourhood. These ties to tradition, however, appear to be weakening. The growing acceptance of plastics in all types of applications in recent years has done much to popularize these materials and to remove resistance by the consumer.

# FORCES FAVOURING GROWTH OF PLASTICS IN CONSTRUCTION

Despite the obstacles that have prevented plastics from being used to their full potential, the future in developed nations appears bright. The following examples illustrate some of the factors at work to help expansion in the United States — in addition to the effect of research and its revelation of new applications and increasing versatility.

#### Civilian consumer pressure

The consuming public — including the private homeowner and the business community — is increasingly accepting plastics as quality and prestige materials, as the result of proven experience and favourable publicity. Recent exhibitions, the latest of which involves extensive structures and displays at the New York World's Fair, have dramatized the versatility and attractiveness of plastics. As plastics build an image as a prestige material with more interesting design and greater dependability, consumer pressure will be a potent factor for growth.

# Government programmes

The United States Federal Government, one of the largest potential customers of goods and services, is pressing for new construction techniques at lower cost. It now owns 350,000 housing units, most of them at military establishments in the USA. The bill for upkeep and operation of homes for military families totals about \$350 million annually. (5) A possible progressive force in introduction of new building materials could be the government building programme. For example, the armed forces planned to construct 7,500 new units in 1963. (5) All military housing is on government land which is free of municipal building codes or zoning regulations.

# Prices

Although advantages other than costs have accounted for the growth of plastics in many applications, further large-scale growth will be highly dependent on costs. The major plastics used in construction have shown a dramatic record of continued price decline for a number of years. One must use extreme care in quoting or comparing prices, especially in the case of plastics; they may vary widely from locality to locality, depending on the formulation and on the level of distribution. With these limitations in mind the numbers in table 6, representing generally quoted prices by primary di vibutors, are shown merely to illustrate these trends and to provide at the same time direct comparisons of plastics with some of the metals used in construction. All plastics have continued to decline in price. Although some contend that the price of plastics will level off, new catalytic techniques for production of raw materials and polymers, as well as the prospect of improved manufacturing methods, promise to bring prices of plastics still lower. It has been predicted, for example, that polyvinyl chloride will be sharply reduced in price as the result of a new technique to produce the monomer. (11) On the other hand, even the most optimistic expect the price increase of some of the metals, such as cold-rolled steel, to continue over the next decade or so. (12)

Although the foregoing comparisons were made on a per-pound cost basis, plastics are lighter than most metals and for a given application might more realistically be compared on a volume basis. The following numbers, involving ABS (commonly used in pipe) provide a comparison: (13)

	Materiai										c/cu in						
ABS .																	1.5
Aluminium	۱.		,						•	•							2.1
Steel (cold 1	rol		d)									•					2.5
Steel (stain)	cs	s)	•	•	•	•				•	•			•	•		13.4

# NEW DESIGN TRENDS AND BUILDING PRACTICES

It can be clearly stated that plastics virtually stand on the edge of many broad new horizons in the construction industry. But, what are the significant influences that will direct the future?

First, the real volume market for plastics is in walls, roofs, partitions, and floors—not in luminous ceilings, decorative laminates, tiles, glues, finishes, and drain pipes, as attractive as these have been. One of the major obstacles, however, is inherent in the tendency to use a new material as a direct substitute. This not only "cheapens" the material in the minds of the consumer but hinders architects and engineers from realizing its full potential. Architects must understand and utilize the unique combination of characteristics of any material. Conventional materials are understood and their characteristics are used to advantage in conventional construction designs and systems. If volume markets for plastics in walls, roofs, partitions and floors are to be

# TABLE 6. PRICE TRENDS

	Cents per pound				
	1950	1960	1964		
Plastics					
Low density polyethylene	44	36	20		
General purpose polyvinyl chloride	37	20	15		
General purpose polystyrene	28	18	15		
Metals					
Aluminium (99.5 %)	17	27	24		
Copper (electrolytic)	22	32	32		
Brass (yellow)	19	24	29		
Steel (carbon billets)	2.6	4.0	4.2		

realized, new and creative construction designs and systems must be developed that exploit the unique weight, strength, æsthetic and other properties of plastics in these applications.

# Architectural and design trends

Although much of the current architectural design tends toward skeleton construction and conservatism toward new materials, the "seed" for change already exists. To better understand the growing acceptance of plastics in the construction industry, it would be helpful to better understand the current trend in architecture and what has led to it.

The manner in which men build has undergone more radical changes during the past century than during many preceding centuries. Although new developments have taken place in almost every field of human endeavour, nowhere has change been more spectacular than in the field of architecture.

Because of the need to employ and house more and more people in large urban centres, builders have had to learn to build vertically. Technology has provided two essential tools: a steel-frame building that can rise to considerable heights without requiring inordinately thick walls at ground level, and the mechanical elevator. With more and more goods being manufactured by mass production on large assembly lines, it has become necessary to roof large spaces with uninterrupted spans; technology has answered this need in terms of steel and glass structures, and more recently in terms of large reinforced concrete vaults.

As these trends continue, we can expect building concepts that have no prototype. As a result, structures will have an element of plasticity requiring building materials with characteristics that will permit them to be molded and shaped to practically any configuration.

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Although the majority of architects in the United States and in other parts of the world are still relatively conservative, there are many that can be considered "innovators". Each one is solving his particular design problem in his own way, developing new design concepts and utilizing conventional products in new applications. Conditions appear very good in this period of change for the introduction of new materials with the characteristics of plastics.

# Construction methods and techniques

The drive to reduce costs is a further factor that promises to stimulate new construction methods and techniques and ultimately to increased use of plastics. Because of increasing competition, the contractor must find ways to achieve a given result with fewer dollars; since World War II, builders have made every effort to make the erection proces faster and more efficient.

Several new engineering developments are helping, not only to reduce building costs, but also to broaden the utility and applications of plastics in construction. For example, fully automatic moulding techniques have been applied to compression, injection and blow moulding; through the use of new machines and ingenious mould designs, completely automatic forming procedures have been introduced. Also contributing favourably to the ultimate cost to the consumer is the fact (but plastic components can perform the function of several other materials. Prefinished sandwich panels for example, can serve as the interior wall, the insulation and the exterior painted wall — at the same time obviating the need for wood studs. Furthermore, very little maintenance is required, such as painting and repairing, when compared with conventional materials such as wood.

Indicative of future possibilities is the announcement of an American Management Association inceting on "Plastics in the Building Industry", to be held in Chicago this Fall. The announcement brochure, directed to architects, designers, builders, contractors, and suppliers carried this message: "Almost everyone in the building trade is aware of the varied uses of plastics in construction today. Their impact is being felt throughout the building trade and industry. Rapid changes in methods and materials often make last year's development: outdated. The only effective way to insure really effective results from the use of plastics is through up-to-the-minute knowledge of new materials and the most modern techniques of using the old ones." The session is designed to bring "... up to date the numerous applications for plastics that are creating a gradual revolution in the building industry".

# NEW PLASTICS APPLICATIONS IN CONSTRUCTION.

Meetings of the type just mentioned — along with the break in traditional design, the acceptance of new materials, and the emergence of new construction cechniques —

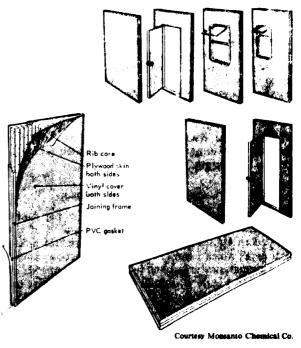
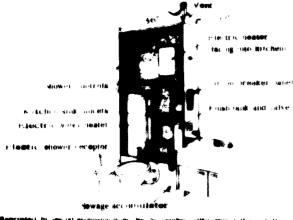


Figure 1. Modular panel



Reprinted by special primitian from the November (1963) and it Home compartmined (1) (964 m. Molinaw Polit Publishing Company Inc

Figure II. Plastic mechanical control for modular wall system

give promise of a dazzling array of new applications of plastics. The following specific examples are intended, therefore only to illustrate the trend.

# Interchangeable modular panels

Plastics have been used in a number of interesting studies with modular units. In the prefabricated housing industry, much of the effort toward preassembled components has consisted of wall and roof panels, doors and frames, and kitchen cabinets. A successful building system of interchangeable wall panels by the Monsanto Company is shown in ligure 1. Essentially dependent upon plastics for its unique features, it also utilizes other materials. Each panel consists of outer skins of a rigid vinyl-based sheet 0.015 in thick laminated to 1/4 in plywood for rigidity. The core, made of 2 in. of polystyrene with kraft paper reinforcing ribs, has excellent structural and insulating properties. The panels are surrounded by edge bands of thin-sheet steel with slots for clips to tie the panels together. A small steel rod provides reinforcing to the panel joint. Finally, an H-shaped vinvl gasket seals each joint. As shown in figure 1, window and door openings can be cut in the panel. Roof and floor panels are identical.

In addition, Rohr Corporation of Los Angeles is currently marketing a 4 ft. by 8 ft. sandwich wall panel for use in housing.

#### Prefabricated mechanical centres

Several builders and manufacturers in the United States, Sweden, Denmark, the federal Republic of Germany, and USSR have developed prefabricated mechanical cores which consist of complete bathroom, kitchen (food preparation areas), and furnace rooms. An example is shown in Figure II. Volume purchasing and high productivity is reducing cost of the mechanical core 25 to 35 per cent (14) below normal cost.

Entire bathroom assemblies have also been fashioned from plastics by the Rohr Corporation. Because of lightweight and unitized construction, this system offers an excellent opportunity for plastics chrough lower handling transportation and installation costs

#### Window gla. mg

Within the last 18 months, the New York City School Board has approved transparent actylic sheet for ese as window glazing to the New York City schools. With this precedent having been established to New York which has a building tode that in many area unds to be a model for other building codes in the Linual States it is likely that this same material will be approved for use as glazing in other areas of the Linued States.

# Loud-hearing elements

The use of plastics for primary structural or external load bearing elements in structures has not appeared practical until very recently. Root panels fabricated of fibre-reinforced plastics serve as an integral roof vectors with provisions for a suspended ceiling.

A United States manufacturer. Joseph P. Ryerson and Son. Inc. recently announced availability of a wide variety of glass-fibre reinforced polyester contours in many standard siructural shapes and sizes. Characterized by compressive strengths of about 20,000 psi, standard shapes include libeams, wide-flange shapes, solid rounds and squares, round and square tubing, channels, angles, and flat and corrugated sheets. These components can he used in the construction of small buildings, for roofing and siding, and for structures in which non-metallic components are mandatory, such as those located in highly corrosive environments. With this major breakthrough in producing plastic shapes for structural framing systems, use of plastics in multi-story buildings could develop into one of the major markets for plastics in developing countries, as well as developed countries.

#### Forms for concrete

Use of plastics as concrete formwork is attracting considerable attention. As architects and engineers learn more about the structural capabilities and limitations of concrete and the fact that it has almost unlimited formability, more experimentation is occurring with sculptured shapes. A recent project in the United States involving plastic formwork is the Marina Tower Apartments in Chicago, Illinois. This project, due to its many curvilinear shapes, required the use of relatively complex formwork. Reinforced plastics were particularly suitable because of their strength, light weight, and capability of being produced in any shape. In addition, all plastic formwork provided improved finished concrete surfaces and easier stripping. Among other significant examples in the United States using plastic formwork may be included such projects as the Earth Sciences Building at the Massachusetts Institute of Technology. This 23-story structure has a wide and finely articulated bearing window wall, and with minor exceptions will be entirely cast in place. A Jewish Temple in Chicago, which consists of eight columns that "blossom" into an umbrella-like design at the roof, also utilizes plastic formwork.

Routhly adapticable to concrete form systems is the hand-layup tibre glass method. By this process liquid rooms are transformed at room temperature into durable solid material by adding a catalyst. When the result arcombined with tibre glass and reinforced with would us inetal the rooalt is a shelf of very high strength with capability of being produced in any shape desired. A cross-sectional view of this type of form is shown in figure 111.



Figure H4. Polyester more plass lavap concrete horns.

Use of polyoster resin for column formwork costs approximately 90 onts per sq. ft. (15) if it is reused at a present practical level of about 20 times. Lumber form work for the same initialitation would cost approximately the same at the normal use rate of four or five times. Even in countries where wood is plentiful, therefore, it is possible at the present time for plantic forms on a large project requiring repetitive uses of formwork to compete with wood on a cost basis to say nothing of the much greater flexibility in design.

# The future as revealed in major exhibitions

During the past few years, there have been a number of outstanding building projects that have used plastics as a major part of the structural finish. The most prominent were those seen by the public at major exhibitions. For example, the Monsanto Company's "House of the Future" on display at Los Angeles, California, uses a rigid frame of glass-fibre reinforced plastic which acts as both structural support and finish for the house.

The United States Exhibition at Moscow in 1959, used a modular umbrella-like reinforced plastic structure. The light-weight unit could be easily shipped and was quickly erected with minimum field equipment. The plastic material offered the designer virtually unlimited shape and form, met the structural test of withstanding wind gusts up to 60 mph, and provided a translucent structure.

The United States Pavilion at the World's Fair in Brussels in 1960 had an exterior skin of translucent plastic also. Although the building was large, the lightness and translucency of the plastic panels provided a vibrant scene at night.

More recently, structures at the New York World's Fair, such as the Bell Telephone Building, utilize an exterior skin of plastic panels. The wing-like exterior of this structure is glass-fibre reinforced polyester panels. The panels, 37 by 12 ft., meant fewer joints, less weatherproofing, and no painting at all. The Brass Rail Restaurant buildings have a series of glass-fibre reinforced s ny bubbles shich provide an unusual and distinctive such

# FOLONIE OF FORME OF AN OF ANOTHING THE CONTRACT OF A CONTRACTOR OF A CONTRACTOR OF A CONTRACTOR OF A CONTRACTOR

The home of institute seconding to some predictions with the essentiality all practice with antirely different construction. Interaschan those dow in effect Cortainly the exploding technology as ident in most advanced economies points to increasing applications for practice is does also the potential market for example the %4%0 million spent or practice in building in 1960 represents only 1 per ent of the total construction follows in the United States (196).

Such factors as the increasing strength to weight (ano newly announced plastics with tayoutable engineering atings and generally increasing levels of performance are potent driving forces as are also the consumer and cost considerations previously mentioned. We realize however that for the immediate future plastics self (on time to be applied mostly to conventional construction (1b) Continual improvements in to biology evolving construction techniques and less restrictive codes will bring the "house of tomorrow" as an evolutionary process.

Whether that evolution will become a revolution only time can tell. If one were to extrapolate the current rate of increase of 10 per cent per year (970 will see three billion pounds used (hgure IV). However: number of projections are considerably more optimistic, including the following.

- Plastics in construction in 1973 will equal the total of all plastics produced in 1963 (16).
- 2. By 1970, the U.S. construction uses will absorb at least four times as much plastics as in 1963 (17)

I here forecasts are spotted in figure IV.<sup>3</sup> along with data on past history, to serve as a base for those who are interested in making their own predictions.

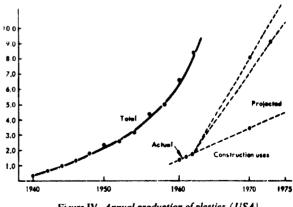


Figure IV. Annual production of plastics (USA)

<sup>&</sup>lt;sup>3</sup> The production figures for 1963 and 1964 used in calculating the predicted values were obtained from the bottom 10 per cent extrapolation curve.

# PART 2. NEX-NEWS NEEDS AND THE BOLE OF PLANTICS IN DEVELOPING ABEAS

# INTRODUC TRON

The present date of development of plastics in the more advanced economies and extrapolation of present riends isoves little doubt of a bright future for their role in construction. To use these present and evolving technologues effectively indeveloping contitues. Nowever, requires an understanding of the new environments within which they must operate to the case of housing and construction the nature and scient of the need must be examined along with the availability of construction materials and skills. Not to be ignored are the impact of existing economic situations and levels of industrialization.

With these factors as background, the following secrions review the strategic geographic location of petroleum as a basic raw material for plastics to be used in construction analyse potential applications of established practices and technologies discussed in part 1 of this paper and project possible new directions for use of plastics in construction to meet the needs of developing countries.

# STATUE OF CONSTRUCTION NEEDS IN DEVELOPING CONTRIES

Few countries have found workable formulas for accomodating their growing and shifting populations If measured by simple need, the unsatisfied demand for all types of construction materials in developing nations exceeds by manyfold existing commercial supplies and will expand dramatically during the next several decades The United Nations estimates that "over 1,000 million people in Africa, Asia, and Latin America. about half the total population of these countries. live in housing which is a health hazard and an affront to human digrity". (19) During the decade 1960-1970, over 200 million new inhabitants are expected to crowd into the cities of Africa. Asia, and Latin America. (20) Problems of housing for rural areas and villages will also demand attention. Several factors are involved.

# Acceleration of population growth

According to United Nations statistics, population growth in developing countries today ranges from about 1.7 per cent annually for Iran to about 3.7 per cent for China (Taiwan). (See appendix 2, table A-1.) The significance of even slight differences in growth rates is impressive. At a rate of 2 per cent annually, a nation will double in population after about 35 years; but a 2.5 per cent increase annually will double the population in about 28 years; 3.0 per cent will achieve a doubled population in about 24 years; and 3.5 per cent in about 20 years.

Furthermore, there is evidence that in recent years the rate of population growth has been increasing for virtually all developing nations that have achieved economic gains and that have improved public health and sanitation For instance Euriley's population growth was about 1.6 per cent between 1927 and 1931, 2.2 per cent between 1945 and 1959, 2.8 per cent between 1959 and 1955 and 2.9 per cent between 1955 and 1966 (21) Decreasing infant mortality and longer life expectancy play a significant role.

# Rural urban shift

Cities an be expected to expand at a rate greater rhan the over all population increase the frend is already well established. The bulk of the world population about 70 per cent is now cural and numerically the source to most of the population increase (appendix 2 rable A. 2). The trend toward urbanization has already been evident in most developing countries as well as developed ones to example both Bogota and Caracas about doubled in a decade. Bogota reaching an estimated 1.256 fifth in 1964 and Caracas, about 1.356.000 in 1959 (22-23) As appendix 2 rable A.3 shows these are typical examples, both numerically or in percentage increase.

The impact on living conditions has been summarized in a study report on housing from the United Nations Office of Public Information in collaboration with the Technical Assistance Board (24) "In the developing nations, where housing must take its place in a long line of economic and social needs, the difficulty has been compounded by the rush from farm to city. At its worst the housing jam spills over into squatters colonies. Hundreds of thousands of homeless exercise the right of possession over neighbourhoods no one else wants. Their numbers are swelled every day by the incoming tide from the villages. And the villages, though by no means in the same straits as the cities are themselves inadequate."

# Replacement of structures

Even the new construction now rising in developing countries is sometimes beset by difficulties. Poor quality materials or inadequate substitutes have to be used at various points in construction. Quality control is not developed and labour is often inexperienced. As a result, walls occasionally tend to crack, plumbing fails to operate properly, and electrical service may be erratic. Thus, the obsolescence of housing is usually more rapid than in industrial societies. Materials must be made available in the future to replace or renovate these structures.

To these problems must be added the devastation which occurs periodically as the result of earthquakes and other natural disasters. In cases such as these, large quantities of materials are required on an emergency basis. The "ed for earthquake-resistant housing is also evident.

# **Rising aspirations**

With broader self-government, industrialization and improved services, there is a growing demand in developing countries for improved housing. At the same time, further extension of mass communication to developing countries — through radio, television, and magazines —

# can be expected to intensify the general demand for higher living standards including improved housing

The governments of developing nations are striving to evolve forward-looking programmes to improve living conditions. Increasing attention by both national and local governments is evident in orban planning. street and park construction sanitary engineering, sum clear ance and provision of improved housing.

An important factor in this movement is the Enited Nations acting as both catalyst and innovator. It has over 10 specialists in all phases of housing and planning working on a variety of technical assistance projects in 18 of the developing countries. At the centre of the organization's housing activities is a small unit in its own secretariat made up of professional staff members from ten countries. Working closely with the United Nations Mousing and Planning Branch they provide both ideas and action. Helping this Branch to keep in fouch with these new developments are the four regional commissions of the United Nations in the Fai Fast Latin America, Europe and Africa. (25)

# THE ENVIRONMENT WITHIN WHICH SHELLTHINK MUST

While some of these pressures for construction are overlapping, we foreser a rising *polinital* demand in the next several decades for construction materials that should far surpass anything experienced since World War II Potential demand, however, cannot be equated with actual demand for products in the marketplace in developing countries, potent economic and technological factors stand between the need for construction and the ability of populations to marshal their resources to satisfy the need. Far from attempting to describe and define these situations in detail, the following paragraphs are designed merely to outline some of the factors to be taken into account.

# Per capita monime

The most obvious harrier can be described as one excessive cost of adequate construction materials and the durthat needed housing is not within the cost of chose that need it most. Developing countries to not take the capital to establish claborate housing schemes not the ourchasing power to material the output of such schemes.

There are two basic means of attacking this problem of clowering costs either by introducing new materials and new technologies or 15 enhancing the abdits of the people to purchase the materials by economic growth Plastics in construction may provide at least a partial answer to both problems as will be developed later.

# Foreign exchange

With the existing real demand for construction materials now exceeding local supplies in many areas the problem of foreign exchange cannot be ignored importation of building naterials means an outflow of valuable capital without any promise that the outflow will someday come Furthermore, modern housing, using conventional materials, requires a wide range of products, which cannot be produced in one or two plants. To build a complex of plants may place an intolerable drain on a local economy. On the other hand, plastics from petroleum can provide versatile products for use in construction. Because the required intermediates are available as a product of other petrochemical operations, the net result can be a significant reduction in the foreign exchange problem.

# Marketing structure

Even if the materials and components for housing cap be manufactured within the country, distribution and marketing systems are essential to housing development. First, transportation facilities can be slow and costly; banking resources may be restricted and difficult and expensive to tap, a nationwide system of billing, credit

Material	North America	South America	Burope	Asia	Africa	Oceania	
Earth based (1962)							
Cement	414.00 M. Bbl.»	79.00 M. BH.	1,158.000 M. Bbl.	371.00 M. Bbl.	50.00 M. Bbl.	20.00 M. Bb	
	16.70 M. s.t.*	0 50 M. s.t.	27.000 M. s.t.	4.30 M. s.t.	1.00 M. s.t.	0.70 M. s.t.	
Asbestos	1.30 M. s.t.	0.02 M. s.t.	1.200 M. s.t.	0.13 M. s.t.	0.40 M. s.t.	0.02 M. s.t.	
Structural Clay Products							
(1962)	28.00 M. s.t.	NA*	NA•	NA•	NA•	NA*	
Wood (1960 U.N.)	435.00 M.C.M.4	154.00 M.C.M.	600.000 M.C.B.	377.00 M.C.B.	122.00 M.C.M.	22.00 M.	
Plywood	9.00 M.C.M.	0.20 M.C.M.	2.300 M.C.M.	2.80 M.C.M.	0.16 M.C.M.	0.13 M.	
iron and Steel (1962)	74.00 M. s.t.	2.80 M. s.t.	162.000 M. s.t.	48.00 M. s.t.	2.80 M. s.t.	3.80 M. s.t.	
Aluminum (1962)	2.75 M. s.t.	0.03 M. s.t.	2.340 M. s.t.	0.33 M. s.t	0.06 M. s.t.	0.02 M. s.t.	
Plastics (1961)	6.80 Bil. lbs.	NIA.	6.250 Bil. 15s.	NA <sup>a</sup>	NA•	NA•	

TABLE 1. HUILDING MATERIAL PRODUCTION \*

Statistics compiled from :

1. U.S. Bureau of Mines, Minerals Yearbook, 1962.

 United Nations, Food and Agriculture Organization, Yearbook of Forest Products Statistics, 1963.

3. Chamical Week, 91 (4), 53 (1962).

• Barrels.

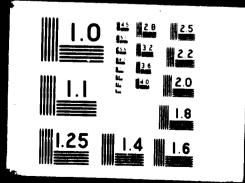
· Short tons

<sup>4</sup> Million cubic metres

• Data not available.

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and checking institutions may require further development; and the business institutions may not adapt readily to mass movement of materials.

The situation is further complicated by a highly fragmented market. In most developing countries, the traditional rural housing varies drastically from region to region, partially for ethnic or social reasons but also because of climatic conditions.

#### Labour

The labout situation in developing countries frequently dictates the types of materials used and the manner of their use. Generally there is a surplus of unskilled workers, usually accustomed to the same type of construction technology prevalent in rural areas. The new technologies, such as electrical circuitry, plumbing, and, in some cases, carpentry, present training difficulties from the standpoint of educational levels of the trainees and the availability of instructors.

The increasingly complex problem of skills in the building of houses has been recognized by the United Nations, and is part of the programme mentioned previously. (26) Recent developments in plastics technology, may provide routes to self-help in construction because a minimum of specialized skills are required.

# **Resources for building materials**

Also of concern is the disparity of resources among nations and the lack of construction materials where they are needed the most. In many of the developing nations, the necessary metals and the forest resources are either lacking or unavailable (table 1), for a number of reasons.

Although mineral deposits are known to exist in many of the developing areas, specific information is generally lacking, and geological knowledge is often scanty. As of 1960, only the United Arab Republic and Israel had been able to arange for a detailed geological survey. (27) Even where ores may be abundantly available, as is the case of Brazil with its huge iron ore reserves, the coal required to produce steel or other metals is often lacking. As a result, development of metal production has been retarded.

Perhaps even more critical for the majority of developing nations is the lack of or shortage of wood for construction. The Mediterranean Basin, which also lacks coal to make steel and cement, has only meagre forest reserves. Nor can the European countries supply the needed lumber for construction. As early as 1956, a United Nations report (28) stated that production of softwoods for Europe was expected to fall considerably short of requirements and that the deficit would have to be covered by heavy imports and an extensive substitution of other materials. This lack also extends in a wide belt across the Middle East into Asia (figure 1). Only Tunisia, with less than one-thousandth of the world's production, is listed among the United Nation's estimates of world roundwood production. (29) Even India, with an estimated fifth of the land forested, (30) must be considered poor in timber resources for a nation with over 400 million persons.

If a nation does possess forests, it may not be able to develop them as readily as petrochemicals for a number of reasons. From the viewpoint of the total economy, it may be more desirable to use the wood for the development of paper or other products, or to export the wood as a raw material needed by other countries. In some cases adequate transportation networks may involve extensive capital outlays, whereas petroleum pipelines already developed can bring the raw material to the place where it will be used or where labour is available. In other cases, technology can be a limitation. For example, the lumbering techniques developed in temperate climates are not applicable to the extensive tropical forests in the

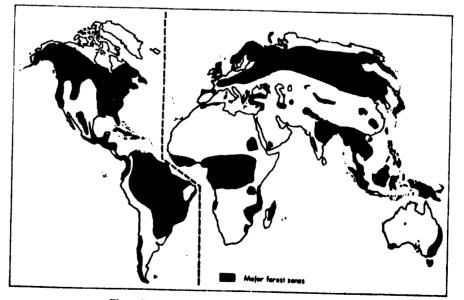


Figure I. World distribution of major forest resources

Amazon Basin; Brazil, meanwhile, imports more than 20 per cent of its wood pulp and 70 per cent of its news-print requirements.

# GENERAL ROLE OF PLASTICS FROM PETROLEUM IN MEETING THE CONSTRUCTION NEEDS OF DEVELOPING NATIONS

Use of plasties as construction materials in developing nations might appear at first glance to be a fanciful and impractical solution. Yet with the present unfilled construction needs and with housing demands sure to become more pressing in the future, an aggressive programme is needed to go beyond present concepts. Such a programme must be geared to use new methods and new materials.

Traditional construction methods and exclusive use of traditional materials will prove completely inadequate. This point has been illustrated by analysis of the situation in Greece. (32) If house construction continues at its present rate, more than 200 years will be required before every Greek can have a home of a quality barely acceptable by today's minimum standards (1.45 persons per room as suggested by Greek architects). Furthermore, dwellings constructed of present traditional materials represent a relatively low standard of living.

Plastics from petroleum present *potential* solutions for fulfilling the needs for construction materials in the environments of many of the developing countries. Pertinent considerations are outlined in the following:

# Availability of petroleum as a raw material

Petroleum, fortunately, is available in many of those developing countries where other resources are scaree or where they have been depleted (figure 11 and appendix 2, table A-4). Because other papers will document this point in detail, the following are to be taken only as examples.

In six territories of the Middle East Iran, Iraq, Saudi Arabia, Kuwait, Qatar, and Bahrain the production and export of petroleum represent major percentages of capital invested, labour employed, and income produced. Jordan, Lebanon, Syria, and the United Arab Republic benefit substantially from the income from of transit. The pipelines across their territories, providing access to oil as a raw material, have led to tl e construction of major refineries. (33) Furthermore, today, we are seeing huge oil and gas discoveries or development of previous lields in all sectors of the globe. Oil and gas strikes in the Sahara Desert have spurred major drilling programmes. Exploration discoveries in Nigeria make that country's offshore prospects look quite promising. Development of oil fields in Bolivia and extension of Colombian oil production to the border of Ecuador have opened up new possibilities in that part of the world. And increased offshore production in the Persian Gulf is expected to bring the total production there to one million barrels by the end of 1964. (See figure 11.) In some eases, petroleum constitutes the largest single raw material for development.

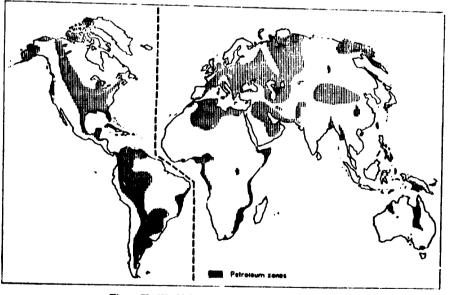


Figure II. World distribution of petroleum resources

One might hope that the rapid growth of the petrochemical industry in developed countries will set a pattern for developing countries. In Europe, for example, only 9 per cent of the organic chemicals were produced from petroleum in 1949; ten years later, the percentage rose to 47 per cent and reached 65 per cent by 1962; in 1965, it should be 80 per cent. Behind this growth is the increasing availability of crude oil and natural gas in Europe.

#### Construction-type plastics from perroleum

Petroleum — whether as crude oil, natural gas, or LPG — is the most economical raw material source for virtually all major plastics except the cellulosics, which are not in wide use for construction purposes. Such processes as cracking, condensation, dehydrogenation, oxidation, and amination can convert the hydrocarbon

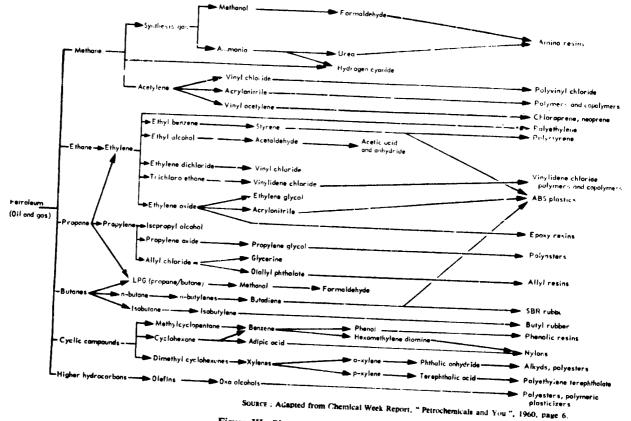


Figure III. Plastics from petroleum

molecules into a variety of intermediates useful for polymer production. Figure III is a flow chart that shows the steps in transformation of various petroleum fractions into finished plastics : not all intermediates nor all potential end-products are shown, but the magnitude of even this listing gives some indication of the versatility of petroleum as a raw material. Further reference will be made to this chart.

The mere availability of petroleum in a given locality, however, does not mean that a successful petrochemical or plastics venture can be launched. If petrochemicals are to be manufactured economically, the co-products from the raw materials must also have adequate markets. Ratios among the various fractions in normal refinery operations are dependent on the source of petroleum feedstocks and the specific refinery operations. To some extent, a refinery can be constructed to adjust product output from a given crude to meet specific market needs. Such processes as cracking, alkylation, catalytic reforming, etc., have been developed to increase yields of desired products. No refinery can operate at peak efficiency, however, if either the feedstock or the desired product mix is varied appreciably.

In the United States, refinery operations are directed primarily toward the production of gasoline, and most of the naphtha fraction is used for this purpose. Nearly 45 per cent of the total output of United States refineries is gasoline. (Table 2 and appendix 2, table A-5.) Conversely, the average gasoline output in Western countries

other than the United States is only about 20 per cent of refinery output. (34) The limited demand for gasoline in  $r_n$  any countries leaves available a rather substantial supply of naphtha for petrochemical manufacture. In those countries where available naphtha supplies far exceed the requirements for petrochemical manufacture, ordinary demand makes naphthas even more of a surplus commodity. The situation is likely to become intensified in the future, reducing the cost of naphtha as a petrochemical feedstock even further.

Fortunately, however, the naphtha fraction comprises a favoured source for plastics as well as other petrochemicals. Indeed, almost unlimited possibilities exist for the production of useful polymer intermediates from the primary chemicals that can be derived from naphtha. Under appropriate conditions, petroleum naphtha yields approximately 25 per cent ethylene, 15 per cent propylene, 15 per cent aromatics, 8 per cent unsaturated  $C_4$  compounds (butadiene and butenes), and a variety of other products. Other processes can be employed to produce mixtures of acetylene and ethylene. Other relatively simple processes can be used to produce the types of intermediates shown in figure III - such as vinyl chloride, vinylidene chloride, styrene, phenol, formaldehyde, phthalic anhydride, and maleic anhydride. Slightly more complex processes can be used for the production of acrylonitrile and ethylene glycol. A very broad range of polymers can be produced from these intermediate and primary chemicals, including alkyd,

 
 TABLE 11. DEMAND FOR GASOLINE VS. ALL PETROLEUM PRODUCTS, 1962

	Demand fo pro (1,000	Gaseline portion of	
Trading area	Tətal	Gasoline	total demand Per cent
United States European Economic	3,733,165	1,583,404	43
Community European Free-Trade	1,108,282	188,087	17
Association British Commonwealth	705,910	142,835	20
of Nations Dependencies of the Uni-	1,023,909	274,570	27
ted Kingdom Latin American Free-	81,160	9,939	12
Trade Association Central American Free-	385,373	104,383	27
Trade Association North Africa and Middle	9,954	2,913	29
East Southern and Eastern	256,760	29,882	i2
Asia, including Japan . Unaligned American	430,410	74,281	17
Countries Central and Southern	130,149	40,839	3.
Africa	58,324	21,383	37
Miscellaneous	154,815	21,535	14

phenolic and vinyl resins, polystyrene. ABS (acrylonitrile-butadiene-styrene), polyethylene, polypropylene, and polybutenes, as shown in figure 111.

# Key properties favouring plastics for construction in developing countries

Introduction of a new material requires a careful analysis of its properties. In many respects, plastics offer inherent characteristics that specially favour their use in developing countries. Not only can they provide satisfactory substitutes for conventional materials that are in short supply; they can also provide superior properties to overcome problems of existing materials and to adapt to the available labour skills. Some of these properties and their pertinence to developing nations are outlined below:

Light weight. Low transportation costs, ease of handling, low structural loading.

Mouldability. Cost savings in fabrication.

- Workability. Low skill levels required for cutting and joining.
- Design flexibility. Adaptability to a variety of configurations to meet loc: astes and requirements.
- Durability (resistance to weather, corrosion, and decay). Lower replacement requirements because of ability to meet extreme environmental conditions.

In addition to these general characteristics, innique properties to meet a special need can be achieved by choice of plastic or by appropriate modifications. Some of these individual characteristics are listed below, to-

gether with an example of a plastic material having the desired property: Toughness polyacetal Hardness ABS (acrylon/trile-butadiene-styrene) Transparency acrylics Vapour impermeability polyvinylidene chloride Structural stability --- reinforced polyesters Impact resistance -- polycarbonates Flame resistance polyvinyl chloride Abrasion resistance nylen.

The foregoing illustrates to only a small degree the versatility of plastics in their ability to replace or to serve as a substitute for conventional building components. Thus, with petroleum as a single primary raw material, plastics have an excellent potential for filling almost the entire spectrum of construction needs in developing countries.

# Role of a plastics construction industry in promoting economic development

Because plastics require industrial facilities for production of primary materials and for subsequent processing, industrialization will be promoted in any country where markets can be created. One of the best *potential* areas for such markets and for large-volume consumption of plastics is in building and construction. Furthermore, development of plastics for use in construction meets the three basic requirements, or objectives, proposed by the United Nations (37) for adaptation of processes and products from advanced countries to developing nations:

- 1. Reduction in capital output to nieet a Jesired need.
- 2. Reduction in import of scarce materials by the widest possible use of substitutes.
- 3. Better utilization of waste materials or by-products (naphthas in this case).

The development of a houling programme car be looked on as a capital-creating resource. With proper planning, the shortage of housing can be transformed from a national liability to a potent force and a new asset in developing the economy. The operation, however, is best approached from two different aspects: (1) a long-range development programme to bring forth a major building industry capable of producing housing of continually increasing quality in continually increasing quantities; (2) an emergency or expediency programme to meet present urgent needs where adequate housing is now lacking.

The expediency programme applies to those who are operating at a bare subsistence level. The savings habit, which makes home-owning possible in most places, cannot be cultivated by workers who live at these levels, using goods to pay for most of their needs. Any improvement has to be made with minimum capital investment. To the greatest extent possible, homes must be built on a self-help basis. Extensive research effort has been devoted to this subject by the United Nations, and the dimensions of such a programme have been outlined and documented in a manual on housing. (35) The self-help potential of plastics in construction promises to become increasingly evident from programmes such as the one at the University of Nuchigan, (36) to be referred to later.

The prospects for generating a building industry involving plastics --- and benefiting from it -- are favourable on a number of counts. As previously outlined, plastics can be made to fit various aspects of the environment. Furthermore, petroleum as a raw material is available in many cases where the need is greatest; and the naplitha in surplus supply from present refinery fraction operations in these countries is a favoured source for manufacture of polymers and plastics. With a versatility ranging from use in the simplest expediency-type structure to the most elegant and costly construction, plastics as building materials can lead to an internal generation of self-sufficiency heretofore impossible. Not only is the problem of foreign exchange ameliorated, but a base for internal economic and industrial development is provided.

#### STEPS REQUIRED TO PROMOTE USE OF PLASTICS IN DEVELOPING COUNTRIES

Up to this juncture, we have developed the following points: the present unfilled needs and future increasing demands for housing in developing nations, the lack of raw materials and specialized skills to meet these needs, the availability of petroleum as a raw material to provide plastics for construction, the existing and proved technology in the more developed countries, the new technologies and expanding vistas for application of plastics to meet building needs of all kinds. The question is one of further translating these raw material and technological assets into a programme to meet the obvious needs.

#### Direct application of existing technology

Many of the examples given in part 1 may find ready translation to building construction in developing nations. The obvious starting place is in the cities with their present large demand. Many of these large cities have well-developed business centres, growing apartment developments, and more advanced residential projects. The modern structures and advanced designs in many cases represent opportunities for *direct* application of the techniques and practices that have been thoroughly tried and proved in past practice.

The use of plastics in such cases might be visualized as a developing ring of concentric circles reaching out from the downtown areas. As industrialization grows, general income levels will rise, providing more demand for permanent high-quality housing.

This part of the programme, potentially significant as it may be, can go only a small way, either volume-wise, or in meeting the massive need for lower-cost housing. It is here that the greatest potential for plastics lies; but it is also the area requiring the greatest care in planning, for it has been found that applying the skills and technologies of developed nations to problems in other geographic areas is not as simple as might be hoped. Many assumptions are erroneous and do not take into account performance requirements for local environments. In developing countries, use of materials must also be translated into the skill levels of the local workers. Most important is the effect of local customs and traditions

including regional architectural characteristics on the acceptance of a different material.

These are factors that have been well recognized in the United Nationshousing programme for developing nations and must be kept in mind in any programme – particularly one involving a departure from traditional materials. With cognizance of these factors, planning in housing might have as its objective the modification of technology already developed and the telescoping timewise of the potential opplication of plastics to the local needs.

#### Advanced total planning --- building standards and codes

In facing the problem of large population centres, an effort should be made to establish metropolitan jurisdictional boundaries along with building standards. With expansion of population centres, land values near the centre of the city increase. Families with limited income move further from the metropolitan area to create an ever-expanding "ring-effect". Proper integrated planning for all areas from the beginning, rather than on a fragmented temporizing basis, can be a potent force for preventing jurisdictional disputes and for promoting adequate housing developments.

As part of the planning programme, building material standards should be established on more than an arbitrary material-approval basis. Proposed specifications should be evaluated to determine whether they are compatible with the prevailing climate and whether they provide consideration of all materials on the basis of functional requirements. An important factor in setting building standards is the ecoromic capability of the people. If al! these factors are taken into account, building codes can be created on a true performance basis rather than on the approval of individual materials. When this occurs, more equitable consideration will be given to plastics, along with other materials.

Since many cities in developing areas have not established a precedant in construction control, this type of planning can provide an excellent opportunity for the use of plastics and for improved quality in housing. Furthermore, adopting codes favourable to plastics may be simpler in this situation than in more developed areas, for developing countries will not face the constraints often presented by the traditional materials industries and labour groups.

#### Use of local materials and skills

As more people move from rural areas to metropolitan areas, they bring many different social customs and traditions with them, including ideas about housing, building materials, and construction methods. These people, in many cases, have established skills in working with materials such as wood, concrete, stone, and stucco. The United Nations' self-help programme has emphasized the need to use or develop these skills to the utmost. Although plastics may represent totally new concepts and new materials, they can go a long way toward promoting the self-help programme and in filling needs that could otherwise remain unsatisfied.

The application of plasties in such local programmes might extend in several directions, especially in residential construction. With proper planning, plasties can effectively augment or replace materials or components: (1) for which a particular skill is not available in the area; (2) where poor quality materials are currently being used; or (3) where there is a scarcity of material. These applications might range from structural and forming members to the wall and the roof, and also include floors, windows, doors, door frames, glazing, insulation, piping, plumbing fixtures --- such as lavatories and sinks, and even preformed bathroom units.

#### CURRENT STUDIES ON PLASTICS FOR BUILDING

Two notable examples will serve to illustrate the attention that has been and is being given to actual applications of plasties to meet special needs of developing nations.

#### **Reinforced plastics in Mexican school construction**

A programme, started in 1960, was designed to complete 2,000 rural schools per year. With the joint efforts of the Mexican government and Vitro-Fibras, S.A., units were designed to supply living quarters. For the teacher, in addition to the required classroom space. Every effort was made to employ local materials and skills. Lacking in most cases, however, were materials for installation of roof, doors, windows, and sanitary services.

The necessary materials have been provided in the form of reinforced plastics according to the following scheme: translucent glass-fibre reinforced window panels are used not only to eliminate the need for costly metal jambs and replacement of broken glass, but also to provide a soft light. Furthermore, they are designed to portray historic Mexican events and educational motifs in pictorial form, giving a stained-glass effect similar to that in many churches. Window vents are fabricated of glass-reinforced acylic polyester resin. To meet cooking and sanitary needs, a unique reservoir, built of reinforced plastic, is placed between the kitchen and the bathroom as a "wet wall". The sanitary fixtures in both rooms are served with a single water feed. Below the reservoir a reinforced plastic unit carries waste water to a septic tank. The accessories, integrally moulded as part of the "wet wall", obviate the problem of assembling on the job; and the single-feed, single-drain system eliminates complicated piping assemblies.

# Michigan University programme on foamed plastics

A project, sponsored by the U.S. State Department Agency for International Development (AID) at the University of Michigan, involves the use of plastic foams in home construction. (38, 39) Principal objectives are to demonstrate that foam can provide both suitable housing for developing countries, as well as the basis for a new industry for those nations. A number of industrial concerns are working with the University of Michigan's College of Architecture and Design in developing foamed plastics for construction purposes.

Basic studies at the University have investigated a number of plastic outerials amenable to fearing techniques and have laid the groundwork for continuing investigation and development.

The first prototype --built to demonstrate a total structural unit, as a follow-up of the initial feasibility study -- was a 45-ft.-diameter dome-shaped house constructed of 4-in, polystyrene. Openings were cut in the foam plastic for doors, windows, and vents. Designed by the University staff, the structure was built by the Dow Chemical Company.

A second prototype – a two-story structure – has been designed to be crected of polyurethane foam board. This material is surfaced on each side with kraft paper and coated with an impregnating material. The prefabricated and shaped boards are joined together with polymeric adhesives, which provide bonds stronger than the original board.

#### FUTURE DIRECTIONS FOR USL OF PLASTICS IN CONSTRUCTION

Future potential uses for plastics in developing countries might cover almost the entire gamut of construction needs. The attractive raw-material picture, the wealth of background from more developed nations, and studies already under way, provide significant assers on which to build. Although much further study will be required - with attention to specialized local backgrounds and requirements - the following examples will serve broadly to illustrate potential applications of plastics in meeting the construction needs of developing nations.

#### Walls and partitions

Because concrete or adobe block is generally readily available to people in many countries, they are reasonably skilled in constructing the walls of their homes. However, because of the need for interior partitions to provide privacy for individual members of families, the construction programme could be accelerated if piastic panels were available at low cost. Not only would cost be an important factor, but the thinness of the plastic panels could be a decided advantage over thick masonry walls, as would ease of construction.

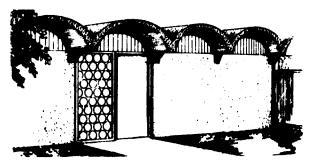


Figure IV. Vaulted foam roof panels

The same advantages will apply in many cases to construction of outer walls. A possible key component for simple self-help homes, for both interior and exterior walls, is foamed-plastic panel-board. This material lends itself well to combination with conventional materials. For example, construction of concrete or adobe block piers can satisfy the traditional desire for stability or permanence; use of plastic panels as curtain walls provides a means for rapid and economical completion of the structure. Extensive research has demonstrated the feasibility of foamed plastics for both dome or panel construction, as previously mentioned

In the course of this work, it was found that either organic or inorganic films or coatings can provide effective surface protection where needed. (40) For example, polymeric films from urethanes, polyesters, or vinyls may be used where a high order of toughness, impact and wear resistance must be imparted. For less stringent demands, foams can be protected with an emulsion paint; for example, latex coatings have given good service.

In some cases, no protective coating is required. (38) Although samples of polyurethane foams submitted to outdoor exposure differed according to formulation, instances have been reported where only discoloration and no erosion occurred on panels exposed for over a year. Where erosion did occur, the affected surface acted as a screen and protected the material bereath — in the ease of panels from both urethane and styrene foam.

The use of plastic panel materials for walls presents not only a low-cost material with excellent insulating properties and utilitarian aspects, but also an interesting possibility for decorative effects through use of colours. A wide variety of shades can be incorporated in the protective film, or in the foam itself, if it is to be used without a protective coating.

#### Roof construction

In many developing countries, roof construction is of particular concern. Roofing materials are expensive, and money to construct the roof is generally hard to



Figure V. Vaulted roof with interior plastic room dividers

find or borrow. Furthermore, considerable skill is required in erecting a frame for the roof and applying the finish. A number of expedients have been employed. A typical roof may use rough-hewn poles as the main supporting element. Over the poles is placed a woven mat, which is then covered with approximately 5 inches of clay. In other eases, the poles may be covered with clay tile and wired in place. In some cases, the poles may have bamboo spanning between them with thatch wired to the bamboo.

The serious nature of the roofing problem has been recognized by the United Nations. In Ghana, for example, a programme has been established to minimize roof completion as a barrier to home construction. (41) Upon proof that a house has been built to wall-plate level, money for the roof is loaned on a credit basis.

In most eases, plastic domes or plastic sandwich panels could simplify the installation, provide a substantial installation, and an improved finish surface. In addition, cost of such a structure could be held to a minimum if manufacturing occurred locally. Figures IV and V indicate a series of foamed vaults which can be used as a roof covering; the walls could be constructed of concrete block with stucco on each side and would support the vaults.

Another design, shown in figure VI, indicates use of structural columns to support the vaulted roof. This design provides the opportunity o erect the structural frame and roof with minimum material and effort; construction might be accomplished as a self-help programme by a local government agency, with the eventual homeowner constructing the panels between the columns. The fill-in panels between columns could be either local materials or a plastic panel, as mentioned previously. Openings between the top of the wall and the underside of the vault could be filled with transparent acrylic glazing for admission of light to the interior in tropical upland areas; an adjustable polyester louvre would serve for cross-ventilation in hot-dry and hot-humid areas.

Manufacture of the foamed vaulted roof sections could be achieved inexpensively by using a Mylar or nylonand-vinyl preformed inflatable bag. Experiments in the Federal Republic of Germany, as well as in the United States, have proven the feasibility and versatility of this method of forming. Polyurethane or polystyrene foam is applied over the inflated bag. Equipment currently available for the foaming operation can apply the foam at the rate of 600 sq. ft. per hour per 1-in. thickness. A 2-in. thick material would support a compressive load of approximately 700 lbs. per lineal foot, which is sufficient to carry a roof load. In order to minimize costs, a reinforcing mesh of local materials could be used and the thickness of the foam might be reduced. If an additional finish is desirable, a suitable coating could be applied. Where conditions are severe, a glass-reinforced polyester could be sprayed over the foam.

#### Windows and doors

An excellent opportunity also exists for plastics in windows, doors, and frames. In many developing coun-

tries where housing is partially put up by the owner, these components are difficult to build because of a lack of tools. By extruding the window and door frames, much the same as aluminum window frames are now manufactured, a relatively small fabricator could supply a large portion of the housing market. The frame could be an extruded polyester, which would include a continuous nylon or polypropylene hinge similar to a in order to reduce stress points on the piano hinge frame after the door is liung. A cross-sectional view of frame, hinge, and door assembly, is shown in figure VII. Doors could virtually be sandwich panels consisting, for example, of polyurethane foam with polyester outer skins on each side. Edges of the door could be covered with a metal channel or with a heavy plastic sheet capable of carrying the weight of the door, once it is attached to the hinge. The door and frame could be marketed as a complete unit or as separate components for installation by the homeowner.

# Water supply and drainage systems

Many cities must consider improving their sanitary and utilities services. Although cement-asbestos pipe provides an economical answer to provision of water mains and sewers, it has serious limitation in housing construction. A major potential use for plastics, therefore, is in the field of metropolitan water supply and drainage systems.

When many new houses are constructed in a relatively short time, plastics can play an important role for several reasons. Cost comparisons in relation to steel and copper pipe favour plastics, as previously shown; and a sufficient number of installations have been made in the United States and Europe to prove the performance of plastics for cold-water supply and sanitary installations (waste, drain, and vent). Relatively large projects could be installed with few skilled workmen, as the material is lightweight and easy to install. In many cases, little more is required than a saw to cut the pipe and a screwdriver to tighten the clamps at joints, or a paintbrush to apply the adhesive. If plastic pipe manufacturing plants are located near larger metropolitan areas, transportation costs could be held to a minimum and the cost of the installed pipe would be low.

#### Sanitary facilities

As economic conditions improve, the desire for more privacy and better sanitary facilities within the dwelling unit will continue to increase. A considerable market, therefore, could develop for plastic lavatories, sinks,



Figure VI. Vaulted foam roof panels

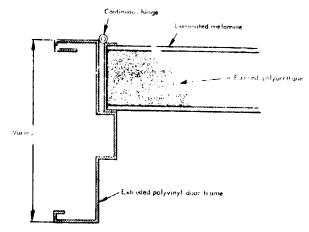


Figure VII. Door and frame

and water closets. These units ordinarily would be manufactured from a glass-fibre reinforced polyester. They can be easily connected to plastic water supply and drainage pipes with a minimum of tools. With a demand for lower cost units, an excellent potential answer is a totally preformed plastic bathroom unit of the type previously mentioned — built to include water closet, lavatory, and tub.

### Structural materials - multiple-dwelling units

A significant aspect of the flight to the cities in developing countries is the strong desire for individual family unite, as a result of the prevalence in most localities of single-family dwellings. However, as urban sprawl increases beyond practical means for transportation, a growing demand for apartments will develop. Metropolitan areas will have to plan for multi-story dwellings, therefore, in order to provide orderly expansion.

With the need for multi-story housing, lack of structural materials could become a particularly scrious problem. As the result of recent developments, however, plastics could supply a large portion of that market in relation to both structural and finish materials. A significant factor, as mentioned in part 1 is the availability of a wide variety of glass-fibre reinforced polyester structural members. These materials are available in standard suructural configurations, with unit tensile and compressive strengths of about 20,000 psi. This major break-

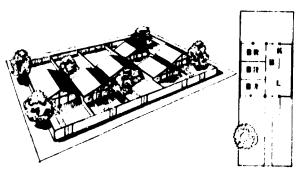


Figure VIII. Foamed rigid-frame row houses

through in producing plastic shapes for structural framing systems particularly in multi-story buildings could result in a substantial market for plastics in developing countries.

# Ail-plastic buildings

The foregoing examples pertain to problems of various building components; but solutions to the total problem are not easy. Cost will remain a key factor. In addition to wider use of self-help programmes, radical changes in housing design are needed if significant headway on low-cost housing is to be made. Such changes have not been made or accepted quickly; generally, it has been an evolutionary process. However, the growth of plastics technology promises to accelerate change in building techniques and concepts, and other pressures will result in a radically different house from those now available. Although the change at first may be gradual, the opportunity for rapid change is potentially greater in developing countries; the significant factor is a lack of precedent in terms of design and of stringent building standards.

The design principles for self-help housing involving major use of plastics are similar to those for any lowcost housing project. They include analysis of lowcost designs applicable to the climate, culture of the area, available materials, and use of the more efficient concepts of mass construction. Particularly important in developing countries is case of expansion and simplicity of construction.

Figure VIII shows a proposed project by Battelle architects for minimum-cost housing, utilizing rigid frames of polyurethane or polystyrene foam with an outer skin of plastic. The panel, which can be manufactured or built on-site, contains both wall and roof. In a large housing development, a grid of local materials could be crected by self-help labour and the plastic foam sprayed on by a single technician who would move from one house to the next. Once the frames are crected or moved to the job site, they can be joined at the roof peak by a locking system incorporated in the panels.

The interior walls, as shown in the plan, can be arranged in any manner desirable, utilizing foamed plastic panels for dividers. End walls to the rigid-frame structure consist of translucent or opaque plastic sandwich panels. In areas where transparency is desirable, as in the living space, an acrylic sheet can be utilized. Expansion of the structures for larger families is possible by adding other rigid-frame units. Additional privacy and security can be obtained by the use of opaque plastic panels surrounding the property. Such panels at a greater distance from the house, together with the transparent panels in the ends of the rigid-frame, will provide a feeling of larger living space.

# CONCLUSION AND RECOMMENDATIONS

The current technology of plastics in construction can serve as a firm foundation for meeting the housing needs in developing countries. Because of their versatility, plastics can be used in conjunction with locally available materials to encourage their use to the fullest extent,

filling the need for construction components or skills that are scarce or unavailable. Where little precedent has been established in rigid building standards, the designer is no longer bound by unreasonable restrictions. Many people, anxious to improve living conditions, are ready and willing to develop new skills. We see now only the glimmer of exciting possibilities that lie ahead. Such components as walls, roofing panels, windows, doors, and even an all-plastic house -- as suggested in this presentation -- can fill major gaps, but these will be only the start.

With these trends, the step now required is to choose a route that will transform established technologies as rapidly as possible to meet local environments and needs. Plastics broadly, and plastics in housing specifically, provide a promising route to industrialization and to the satisfaction of these needs. Because they represent a potential for one of the largest single-volume outlets for petrochemicals, they provide on the one hand an incentive and an encouraging factor for building and expanding refineries into petrochemical production. On the other hand, because plastics themselves require industrial facilities for manufacturing and processing, they can help to promote industrialization as their markets develop.

Despite the potential for providing a route to selfsufficiency in meeting housing needs via plastics, careful attention will be required on several fronts to insure realistic industrial development. Prices for plastics used in construction have reached their present attractive levels, not only because of technical developments, but also because of increasing production capacity. To set up a complex of small plants in each developing country to produce a spectrum of polymers and plastics could prove uneconomical.

The importance of large volume production by newly industrializing countries was stressed in a presentation to the Third Arab Petroleum Congress in 1961, with the admonition that the development of a petrochemical industry by a group of developing nations "seems only feasible on the level of both an internal common market and a sizable export prospect". (42) The advantage of large-volume production might be realized by construction of one — or at most, only a few — large-volume plants in a given country to produce a given group of polymers and plastics; by trade agreements with other countries manufacturing other products on an equally large scale, a mutual cost advantage could be realized.

More than a passive programme will also be required to translate established practices and present uses for plastics in construction to the needs of developing nations. Each country or locale should be considered a case unto itself, with its own peculiar problems. Direct applications or adaptations that can be made to meet local environments merit special studies. The United Nations might become a most effective medium for co-ordinating existing technology and for guiding acquisition or development of new technologies to meet local needs. Widespread promotion of self-help programmes already estabilished by the United Nations should be encouraged, with special attention to plastics and their role in promoting such programmes.

The early establishment of building standards and codes can go a long way toward premoting, rather than hindering the use of plastics in construction. More research is needed to serve as a basis for establishing specifications and quality requirements for given areas, with special attention to adjustment for local climatic conditions. To provide assurance that these materials will prove satisfactory in their new environment, the trial and error method is to be avoided. A programme involving controlled exposure studies at the site involved is highly desirable, especially where unusual conditions are likely to be encountered. Special emphasis should be given to those forces that are likely to cause damage to building materials, such as solar radiation, high temperatures, moisture, atmospheric pollution, insects, and rodents. Further attention should also be given to fireproofing agents or to fire-resistant plastics.

By building on the present firm foundation and with proper planning and effort, we should find future opportunities for plastics in developing countries to be almost unlimited.

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#### APPENDIX 1

TABLE A-L. MAJOR PLASTICS IN CONSTRUCTION

Plastics in common use for construction today

ABS (acrylonitrile-butadiene-styrene):

Excellent resistance to chemicals; impact strength, hardness, abrasion and heat resistance—used for drain, waste and vent pipe, pump parts

- Acrylics:
  - Strong, clear, good weatherability -- used largely for glazing, light diffusion, skylights, decorative applications. Available as cast and extruded sheet. Foamed products are being developed, having an added insulation property
- Alkyd moulding compounds:

Electrically insulating --- moulded electrical parts

Alkyd polyesters:

Tough, flexible, used extensively for coatings on metal, wood, masonry

Cellulosics:

Original plastic discovered in mid-1800's. Characteristics vary widely. Cellulose acetate butyrate is tough, weatherresistant, clear. Used for exterior applications, store facades, pipe, knobs, buttons, instrument housings

#### Coumarone-indene:

Water-resistance additive -- used in coatings such as concrete scalers, wall paints and primers, asphalt tile, vinyl-asbestos tile

#### Epoxies:

Adhesive, hard, strong, weather and chemical resistant, electrically-insulating, heatable. For concrete patching, caulking, simulated tervazzo, protective coatings, electrical insulation, sealants, adhesives, laminates

# Melamine and urea:

Dimensionally stable, heat-resistant, durable and presenting an unusually hard surface used extensively for lighting fixtures, coatings, ventilator grills, electrical insulators, adhesives, finishes and decorative laminates

#### Nylons:

High strength, low friction — in hardware as bearings for butt hinges, drapery slides, tracks, rollers and guides for sliding doors and cabinets, lock inserts. drawer pulls, door handles, latches, fasteners, window glides; where light weight and smooth operation are required. Nylon also is being considered for use as hot-water plumbing and tests indicate that this is a practical, if relatively expensive, application

#### Phenolics:

Impact resistant, tough, adhesive, chemical and heat resistant, electrically insulating : moulded drawers, electrical insulation, protective coatings, bonding agents, pulleys, handles dials, knobs, laminates

# Rigid polyvinyl chloride:

Non-combustible, opaque or translucent, hard, chemical and corrosion resistant, flexible. Used for partitions, sandwich panel skins, curtain wall skins, pipe, side and sky lighting: complete enclosures, fences, glazing

# Plasticized PVC:

Durable, flexible, self-extinguishing, electrical and chemical resistant, abrasion resistant--used for wire coating, floor and wall coverings, coatings, sheet and film

#### Polyesters:

Tough, strong, clear; weather, chemical and corrosion resistant, high strength to weight ratio. Used extensively with reinforcement for interior partitions, sky and side lighting, sandwich panel skins, patching compounds, coatings, used experimentally as the entire shell of structures.

# Low molecular weight polyethylene:

Strong, tough, flexible, clear — used for vapour and water barriers, waxes

# High molecular weight polyethylene:

Tough, impermeable, corrosion resistant, high strength relative to weight — used for cold water pipe, irrigation, electrical insulation, tools, wire coatings

#### Silicones:

Weather and oxidation resistant, water repellent, excellent electrical properties — used in paints, varnishes and other finishes, masonry water repellents, wire coating, laminating and bonding, caulking, sealing, lubrication compounds, adhesives

#### Polystyrene:

A variety of characteristics — such as high strength, clarity, weatherability — is possible in styrene depending on modification. High impact styrene is used for wall tile, light fixture parts, electrical insulators

#### Expanded polystyrene:

Excellent thermal insulation and water resistance — used in slab form for masonry, roof and perimeter insulation, sandwich panel cores

#### Polyurethanes:

Variety of characteristics, depending on formulation. Flexible foamed urethane is used for cushioning, weather stripping. Rigid urethane foam is used primarily for sandwich panel cores, thermal insulation in masonry, pipe, roof and allied applications (highest thermal efficiency). Urethane coatings display high abrasion and weather resistance, hard surface high gloss and long life. Urethane elastomers are used for drive belts, pump housing linings, gaskets.

# TABLE A-2, PROPERTIES OF TYPICAL PLASTICE \*

	Tonolio strength, pol	Compressive strength, pol	j 20 D impues stremeth fs.W./w. of noich	Hous deflection, tomperature at 264 pd, *P
Thermoplestics         ABS         Acrylics         Polyethylene III         Polypropylene         Polyacetal         Nylon	5,100- 8,000 7,000-11,000 4,000 500 6,000- 7,000 10,000 7,000-12,000	6,400-10,000 11,000-19,000 3,200 8,300-10,000 8,300- 9,600 5,200 6,700-13,000	1.4 0.3-0.5 3  1.0-14 1.4 1.0-3 5	196-215 150-210 (66 pei) 120 150 155-160 212 308-349 (66 pei)
Laminates (Thermosets) Polyester glass Epoxy glass	30,000-50,000 24,000-60,900	25,000-50,000 50,000-70,000	5, <b>0-30,0</b> 40-40	358-400 358-409

Ogden, P., and Hugo, L. A., Phillips Petroleum Corp., Private Communication, 1964.

TABLE A-3. SUPPLY, WARTE, DRAIN, AND VENT PLUMARNO APPLICATIONS - APPROXIMATE MATERIAL COPT IN BOLLARS PER LINEAR PROT (1964)

-	Cer	Copper			Plastic				
Sise, inches	Interior	Drain wate &	Cast Iron	Galvanized steel	Palyer	Ay tone		Polevineri chiarai	•
		149 <b>10</b> 7			100 pai *	<b>10 put *</b>	PVC 100+	Schedule 40 4	Schedule #
1/4	0.15	0.08	_	0.13					
1/2	0.26	0.13		0.18	0.05	0.05	0.11	0.16	0.21
3/4	0.41	0.21		0.23	0.09	0.07	0.13	0.22	0.29
1	0.62	0.31		9.33	0.15	9.12	0.17	0.34	0.43
I <b>-1/4</b>	0.56	0.44	_	0.43	0.25	0.20	0.22	0.45	8.59
I-1/2	1.10	0.55		0.50	0.32	0.27	0.29	9.54	0.72
<b>1</b>	1.72	0.86	_	6.72	8.60	0.40	0.45	0.73	1.60
2-1/2	2.45	1.23	_	1.06		0.69	0.65	1.16	1.44
<b>)</b>	3.12	1.56	_	1.44		1.07	0.96	1.51	2.00
•	5.10	2.55	1.50	2.16			1.60	2.16	2.97
<b>5.</b>	-	_	2.25	3.72		_	3.44		4.91
<b>.</b>		_	3.35	4.86		_	3.++		
0		-	4.45	-	_	-	_		

Note : Data provided by Colanese Plastics Company, July, 1964.

Polyothylone pipe capable of withstanding 100 pai at 74-F.
 Polyothylone pipe capable of withstanding 80 pai at 74-F.
 Polyothylone pipe capable of withstanding 80 pai at 74-F.
 Polyothyl chloride pipe capable of withstanding maximum pressure of 300 pai for 1/2-iach pipe; 240 pai for 3/4-inch pipe; 200 pai for 1-iach pipe; and 100 pai for pipe; 1-1/4 inches and lenger. Maximum temperature for these pressures is 73-F.
 Polyvinyl chloride pipe capable of withstanding maximum pressure of 600 pai for 1/2-iach pipe; 400 pai for 3/4-inch pipe; 430 pai for 1/2-iach

pipe; 367 pei for 1-1/4-inches pipe; 330 pei for 1-1/2-inch pipe; 276 pei for 2-inch pipe; 302 pei frr 2-1/2-inch pipe; 262 pei for 3-inch pipe, 222 pei for 4-inch pipe. Maniatum temperature for these pressures in 73-F.

73°F. \* Polyvinyl chloride pipe capable of withstanding maximum pressure of 830 pei for 1/2-inch pipe; 600 pei for 3/4 inch pipe; 630 pei for 1-inch pipe; 520 pei for 1-1/4-inch pipe; 470 pei for 1-1/2 inch pipe, 480 pei for 2-inch pipe; 370 pei for 3-inch pipe; and 320 pei for 4-inch pipe. Maximum temperature for these pressures in 73°P.

### APPERMENT 2

Country	Ber. 1964 pagadation (reditions)	Betterstel rate of attend harden	Bonatto 1961 ( pap./km²)
1. Algeria	10.4	1.9	5
1. Congo (Dumostule Republic of)	14.5	2.4	6
3. Bihispin	21.6	-	17
4. Morece	11.9	1.8	27
5. Nigaria	35.8	1.9	39
6. South Africa	16.2	2.6	13
7. 9uden	12.1	2.8	5
8. United Arabic Republic	26.6	2.5	21
9. Canada	10.3	2.2	2
18. Munico	36.1	3.1	36
1. United States	<b>388.7</b>	1.7	7
12. Arguntina	29.1	1.7	
3. <b>Brani</b>	73.1	3.6	9
	14.4	2.2	13
<b>13. Peru</b>	18.4	2.0	•
<b>K. Burns</b>	21.5	2.1	22
17. Cuplum	10.2	1.7	190
IC. Alghanistan	13.0	3.0	21
19. China (mainland)	645.5	2.4	72
20. China (Talwan)	11.0	3.7	200
<b>28. India</b>	448.0	2.3	138
28. Indonesia	96.7	2.3	<b>#</b>
<b>3. hun</b>	38.7	1.7	13
<b>34. Jagan</b> a	94.0	6.9	204
2. North Koren	38.8	2.0	199
26. Republic of Korns	38.4	2.9	200
<b>27. Publishum</b>	94.5	2.1	100
8. Philippins	28.7	3.3	96
2. Thelead	27.2	3.0	38
18. Turkey	28.4	2.0	<b>37</b>
3. Nuch Vis-Ham	16.7	2.1	185
21. Republic of Vist-Ham	14.5	3.9	
28. Cumbertervelte	13.6	6.7	100
<b>34. Premier</b>	-	1.0	
1. Indure Communy	16.0	64	10
25. Pedaugi Republic of Germany	940	1.8	307
SI. Matury	10.0	6.5	
		a.j	105
	14.6	13	346

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TABLE A-1. POPULATION CHARACTERISTICS FOR NATIONS EXCERDING 10 MELISON POPULATION

Country or area	Year	Population (thousands)	Per ceni	Population (thousands)	Per cen
<b>Ngeria</b>	1948	1.838	23.6	5,949	76.4
	1960	3,314	32.5	6.891	67.5
Jnited Arab Republic		-,	2.3	0,091	07.5
(Egypt)	1947	5,712	30.1	13.255	69.9
	1960	9,719	37.7	16.052	62.3
enya	1948	271	5.0	5,135	95.0
	1962	660	7.6	8,013	93.0 92.4
unisia	1946	965	29.9	2.265	70.1
	1956	1.347	35.6	2,436	64.4
ioneeno	1950	1,609	19.0	•	
	1960	3.411	29.3	6,844	81.0
	1951			8,215	70.7
	1951	61,875	17.3	295,004	82.7
		78,836	18.0	359,772	82.0
<b>14</b>	1947	1,628	33.8	3,188	66.2
	1 <del>9</del> 57	2,486	39.2	3,854	60.8
skisten	1951	8,663	11.4	67,179	88.6
	1961	12,295	13.1	81,425	86.9
writery	1945	4,687	24.9	14,103	75.1
	1955	6,927	28.8	17,137	71.2
ienico	1950	10,983	42.6	14.807	57.4
	1960	17,705	50.7	17,218	49.3
	1950	18,783	36.2	33,162	
	1960	31,991	45.1	38,976	63.8
18.	1952	3.561		•	54.9
	1963	6,045	<b>59</b> .9	2,380	40.1
		•	67.2	1,983	32.8
	1945	348	29.0	852	71.0
	1961	575	30.5	1,309	69.5
erto Rico 🛛	1950	895	40.5	1,316	59.5
	1960	1, <b>039</b>	44.2	1,310	55.8
menuela	1950	2,709	53.8	2,325	46.2
	196)	5,079	67.5	2,445	32.5

TABLE A-2. URBAN-RURAL DISTRIBUTION OF POPULATIONS IN FIFTEEN DEVELOPING COUNTRIES

Sounce : United Nations, Demographic Yearbook, 1955, p. 185. United Nations, Demographic Year-

_		-					
TABLE	<b>A-3</b> .	T V PICAL	URBAN	GROWTH	IN	DEVELOPING	COUNTRIES

Chr	Consu unit	Your	Population	Chy	Consue unit	Year	Population
Aren	City	1946	135,926	Karachi	Metropolitan	1951	1,126,417
		1960	337,828			19 <b>59</b>	2,060,690
Algions	Metropolitan	1946	488,893	Lagos	City	1952	267,407
		1960	883,879		-	1962	394,000 *
Ankers	City	1950	298,536	Linne	Metropolitan	1955	1.045.000 *
		1900	646,151			1961	1,715,971 •
<b>Desident</b>	Matematics	1947	899,538	Manila	City	1948	983,906
		1900	1,330,153			1960	1,138,611
Deasta	Clay			Rio de Jaceiro	City	1950	2,303.063
		1951	648,324 *		UN Y	1960	3,223,408
• • • • •		1961	1,256,640 *	Selicitury	Metropolitan	1946	69,100
Button Aires	Motropolitan	1947	4,003,035		Monopolitik	1959	271,000
		1940	7,000,000	Sen Salvador	<b>6</b> 44		
Caire	Chr	1947	2.098.454		City	1950	161,951
		1968	3,348,000			1960	241,318
Chemene	Materiality	1990	493,896	Sentingo	Metropolitaa	1 <b>952</b>	1,348,283
		19:59				1960	1,900,000
Number of Street			1,396,000	See Paulo	City	1990	2,917,025
Djalasta	Chay	1955 1961	1,845,899		-	1960	3,164,804

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# TABLE A-4. WORLD PRODUCTION OF CRUDE PETROLEUM AND NATURAL GAS, 1962 •

### TABLE A-4. (continued)

	Crude petroleum (1,000 barrels) <sup>b</sup>	Natural gas (1,000,000 cubic feet)
United States	2,676,185	13,876,622
European Economic Community		
France	17,071	176,886
Federal Republic of Germany .	48,946	17,970
Italy	12,308 14,742	266,832 22,392
	93.067	484,080
Survpean Free-Trade Association	33,007	
Austria	16,694	61,013
United Kingdom	820	
	17,514	61,013
COMECON		
Albania	4,937	
Bulgaria	1,460	
11	1,150 12,208	N.A. 4 12,674
Poland	1,502	30,625
Romania	88,420	329,805
USSR	1,357,800	2,649,720
	1,466,477	3,022,824
atin American Free-Trade Associa- tion		
Argentina	98,154	N.A. 4
Brazil	33,401	19,082
Chile	11,690	132,844
Mexico	111,830	371,225
Peru	21,134	42,320
ritish Commonwealth of Nations	276,209	565,471
Canada	244,139	946,860
India	7,337	N.A. 4
New Zealand	4	5
Nigeria	24,624	
Pakistan	3,338	42,076
United Kingdom	820	
	290,262	955,941
Barbados	28,286	120 N.A. 4
Trinidad and Tobago	48,877	29,749
	77,163	29,869
forth Africa and Middle East	//j100	23,003
Algeria	158,094	13,189
Bahrain	16,446	_
Iran	481,939	107,161
Iraq	366,832	N.A. 4
	1,126	39,619
Kuwak	758,331	_
Libya	67,052	
	968	N.A. 4
Quier	67,911	—
Sama Ambia	555,056 5,551	_
Soudi Arabia		
Trucial States	5,551	941
Trasial States		267
Trucial States	4,159 52,321	

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Southern and Eastern Asia		
Burma	4,366	440
Indonesia	167,771	95,767
Japan	5,316	45,137
China (Taiwan)	14	1,433
	177,467	142,777
Unaligned American Countries		
Bolivia	2,911	
Colombia	51,918	31,107
Ecuador	2,573	_
Venezuela	167,954	194,363
	1,225,356	225,470
Central and Southern Africa		
Angola	3,404	
Congo (Brazzaville)	926	
Gabon	5,992	328
Senegal	3	
	10,325	328
Miscellaneous		
China (mainland)	51,100 °	
Cuba	90 °	_
Netherlands New Guinea	917	
Yugor!avia	10,785	3,557
	62,892	3,557

• Derived from : 1962 Minerals Yearbook, Volume 11, Fuels, Bureau of Mines U.S. Department of the Interior, U.S. Government Printing Office, Washington (1963).

» 42-gallon barrels.

· Estimated.

<sup>d</sup> Data not available.

# TABLE A-5. DEMAND FOR GASOLINE AND ALL PETROLEUM PRODUCTS BY COUNTRY, 1962 \*

Troding area	Dema petrologi (1.000	Gasoline perilen of	
	Total	Gaseline	per cent
United States	3,733,165	1,583,404	43
European Economic Commu- nity			
Belgium and Luxembourg .	77,881	13,510	17
France	262,562	56,334	21
Greece	24,310	2,458	10
Italy	243,673	35,282	15
Notherlands	141,531	10,852	8
Federal Republic of Ger-	•	Ţ	
many	358,325	<b>69,65</b> 1	20
	1,108,282	188,087	17 •
European Free-Trade Associa-			
Austria	27.642	6,368	23
Denmark	52,355	11,035	21
Finland	25,088	3,760	15
Norway	29,263	5,368	18
Portugal	14,964	2,102	14
Sweden	107,763	19,032	18
Switzerland	35,490	8,995	રડ
United Kingdom	413,345	\$6,175	21
	785,910	143,865	201

# TABLE A-5 (continued)

Trading area	Demai petroleum (1,000		Gasoline portion of total deman	
· · · · · · · · · · · · · · · · · · ·	Total	Gasoline	per cent	
Central American Free-Trade Association				
Costa Rica	1,579	510	32	
El Salvador	1,686	565	34	
Guatemala	3,521	894	25	
Honduras	1,658	383	23	
Nicaragua	1,510	561	37	
teste durat monora	9,954	2,913	29 b	
Latin American Free-Trade Association				
Argentina	110,665	22,670	20	
Brazil	114,659	34,815	30	
Chile	19,154	6,577	34	
Mexico	106,147	30,859	29	
Paraguay	922	337	37	
Peru	21,989	6,621	30	
Uruguay	11,837	2,504	21	
ritish Commonwealth of	385,373	104,383	27 <sup>b</sup>	
Nations				
Australia	90,212	40,888	45	
<b>Canada</b>	335,065	112,302	34	
Ceylon	4,899	1,292	26	
Cyprus	2,288	536	23	
Ghana	3,909	1,192	30	
India	66,349	9,002	14	
Malaysia	63, <b>60</b> 7	9 <b>,746</b>	15	
New Zealand	15,152	8,635	57	
Nigeria	6,272	2,250	36	
Pakistan	20,021	2,344	12	
Sierra Leone	2,790	208	8	
United Kingdom	413,345	86,175	21	
	7,023,909	274,570	27 Þ	
Aden	28,369	3,042	11	
Berbudos	1,511	222	15	
Guince	1,785 2.483	838	47	
British Honduras (Bolice)	122	194	8	
Cameroon	1,018	51 <b>439</b>	42	
Fiji	966	253	43 26	
Hong Kong	10,837	620	6	
Jamaica	5,930	856	14	
Kenya	6,170	976	16	
Malta	1.074	239	22	
Tanganyika and Zanzibar	2,314	676	30	
Trinidad and Tobago	17,538	1.073	6	
Uganda	1,043	460	44	
orth Africa and Middle East	81,160	9,939	12 Þ	
Algeria	7,271	2,776	38	
Bahrain	12,139	558	5	
Iran	53,422	4,218	1	
Iraq	17,555	2,393	14	
Israel	17,288	1,962	11	
Jordan	2,531	328	13	
Kuwait	36,485	2,505	7	
Lebanon	12.056	2,655	22	

TABLE A-5. (Continued)

Libus			
Libya	1,626	567	35
Morocco Snudi Anabia	6,847	2,126	31
Saudi Arabia	23,182	1,876	8
Syria Tunicio	5,764	750	13
Tunisia .	4,411	614	14
Turkey	16,764	4,373	26
United Arab Republic	39,419	2,181	6
	256,760	29,882	12 •
Southern and Eastern Asia			
Burma	4,278	1,310	30
Cambodia and Rep. of Viet-		.,	50
Nam	6,769	2,279	34
Indonesia	40,007	8,298	21
Japan	326,139	48,243	15
Rep. of Korea	7,007	680	10
Laos	239	185	77
Philippines, Republic of	24,783	8,110	33
China (Talwan)	9,154	1,772	19
Thailand	12,034	3,404	28
	430,410	74,281	17 ه
Unaligned American countries			
Bolivia	2,492	1,081	43
Colombia	23,402	11,517	50
Dominican Republic	2,673	868	33
Ecuador	5,623	1,555	28
Haiti	756	281	37
Panama	8,962	1,954	22
Puerto Rico	23,725	7,616	32
Surinam	2,413	149	6
Venezuela	60,103	15,818	26
	130,149	40,839	31 0
Central and Southern Africa			
Angola	2,402	474	20
Congo, Republic	2,648	1,588	60
Ethiopia	960	712	75
Gabon	312	95	30
Liberia	459	218	48
Malagasy Republic	1,078	508	47
Mozambique	2,364	300	13
Rhodesia and Nyasaland,	_,		
Federation of	4,768	2,373	50
Somali Republic	150	50	33
Somaliland, French	9,805	131	1
South Africa, Republic of	29,610	14,200	48
Sudan	3,768	734	19
	58,324	21,383	37 Þ
Miscellaneous			
Afghauistan	1,100	807	73
	2,478	297	12
Iceland		3,064	23
Ireland	13,187		
	13,187 82,048	7,738	8
1reland	•		8 42
Ireland	82,048	7,738	-
Ireland	82,048 364	7,738 152	42
Ireland	82,048 364 568	7,738 152 156	42 27

Derived from : 1962 Minerals Yearbook, Volume II, Fuels, Bureau of Mines, U.S. Department of the Interior, U.S. Government Printing Office, Washington (1963).
 Average for the area.

