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CHEMICALS FROM PETROLEUM - RECENT INDUSTRIAL TECHNOLOGICAL ACHIEVEMENTS OF SIGNIFICANCE TO DEVELOPING COUNTRIES

Contribution by the United Nations Centre for Industrial Development to the General Report, Petroleum Committee Seventh Session (September 1966) International Labour Office

I. Introduction

1. For the purpose of this report the petrochemical industry is defined as that segment of the chemical industry producing chemical products from raw materials of petroleum origin.[1/] According to this definition, raw materials, intermediates and end products like: nitrogenous fertilizers, plastics, synthetic rubbers, synthetic fibres, etc. are all included.

2. The technology utilized in petrochemical production is that of the petroleum and chemical process industries. It has been jointly developed by the chemical and oil refining industries which are the main contributors to output in this sector. On account of this, petrochemical technology is similar to that of those chemical industries which manufacture their products in a continuous process under carefully controlled conditions. One of the contributions of petroleum refining has been in the adoption of the very high scales of production common to that industry.

3. Although the United States' industry has been so far the major contributor to the development of new petrochemical products and processes, European laboratories have produced some of the older, though important petrochemical syntheses.[2/] More recently Japan, whose petrochemical industry only became significant as late as 1955, is also rapidly becoming a contributor of new technology.

4. It should be stated, however, that the petrochemical industry is continuously undergoing technological change. New products and processes replace old ones, and new uses are discovered for existing products.

[1/] In this context petroleum includes both oil and natural gas.

[2/] Among the most important petrochemical products which originated in the European chemical technology are: synthetic ammonia, synthetic detergents, polyurethanes, polyvinyl acetate and alcohol, polyvinyl chloride, nylon-6, synthetic rubbers: BUNA-N and BUNA-S, and oxo-alcohols in Germany; polyethylene and polyester fibres in the United Kingdom; polyacrylates in the United Kingdom and Germany; synthetic fatty alcohols and acids in the USSR and Germany.

5. This technological change originates from organized research and development. The accelerated rate at which new products and processes are developed, together with the reduction of the economic life expectancy of existing products and markets, requires substantial new capital investment to utilize the new technologies. The petrochemical industries rank, in the industrialized countries, among those having the highest expenditures in Research and Development. There is also a distinct trend towards increasing the proportion of research expenditure to total capital investment in these industries.

II. Review of Recent Achievements in Industrial Technology in the Production of Chemicals from Petroleum and their Significance to Developing Countries

6. Research and Development in the industry producing chemicals from petroleum is conducted along two generally broad lines: discovery of new and improvement of existing petrochemical products and petrochemical processes. Scientists and engineers develop in the laboratory, new chemicals from petroleum and natural gas raw materials or improved methods of synthesizing chemicals hitherto available economically only from other sources. This activity is generally designated as petrochemical product research. Experimental laboratory products are then scaled up to large bench-scale, pilot-plant and semi-works stages and finally to full plant production (petrochemical process development). Within these two generally broad lines one finds sub-categories of Research and Development devoted to various specific needs which a particular industrial organization or research institute may wish to emphasize.

1. Raw Materials

7. Hydrocarbons constitute essentially all the feed stock for a refinery with other chemical compounds being present in crude oil only in much lesser amounts. Similarly, hydrocarbons provide most of the raw material used by the petrochemical industry.

(i) Paraffins

8. 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. A most recent development is the controlled oxidation of propane at high temperatures with rapid quench to produce acetylene which may be converted to vinyl chloride, acrylonitrile and other organic chemicals. In steam reforming or partial oxidation process, also recently developed, mixtures of carbon monoxide and hydrogen are produced from methane and used either as such or again reacted with steam to convert the carbon monoxide to carbon dioxide. The latter can

then be extracted leaving hydrogen for ammonia synthesis. One of the well developed processes which falls in the above categories utilizes methane from natural gas for the production of acetylene, and is known as the BASF - Sachese process. It is based on controlled oxidation in deficiency of the oxidising medium to prevent oxidation from proceeding to completion. This feature provides the energy for the main reaction which yields acetylene from methane. The advantageous feature of this process is that the by-product gas contains a substantial proportion of hydrogen and carbon monoxide which together with nitrogen from an air separation unit form a suitable basis for ammonia production. This provides a possibility for project integration in a petrochemical complex in a developing country, i.e. acetylene, synthesis gas, oxo and Fischer-Tropsch reaction products, ammonia and fertilizer production all become feasible in such an integrated petrochemical complex. A recent improvement in the aforementioned process, which has particular value in developing countries, uses a re-designed version of the mechanical equipment (burner and quench assembly) and liquid ammonia as a selective solvent. This version of the process can be adapted to the simultaneous production of acetylene and ethylene which offers an economic advantage. It also allows for the use of heavier naphtha fractions as feed stock which are more generally available in developing countries.

(ii) Natural Gas

9. Natural Gas as a raw material in the petrochemical industry and its importance to developing countries can rightly be the subject for a separate paper. It is important, however, to mention even briefly in this instance a recent technological discovery; 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 corrosion proof materials to establish economic procedures for liquefaction, transportation, storage and regassification. 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 at room temperature. However, the storage container must be heavily insulated so that these low temperatures can be maintained continuously. The significance of this development can be appraised when we bear 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 feed of gas have been flared in Saudi Arabia since oil production was first initiated. This represents, for example, more than the total proven reserves in Alaska. Vast amounts of gas are flared in Venezuela and the Middle East alone (3,700 mmcfd). All indications point to the paramount significance of this technological development. For instance, initial shipments of liquified natural gas in 1964 to the U. K. from North Africa are estimated at 100 mmcfd. A similar amount for 1965 to the U.K. will be followed by 50 mmcfd to France and 30-50 mmcfd to Japan. It is projected that by 1965 ocean transport of liquified natural gas could range from 1,500 mmcfd to 24,000 mmcfd with Western Europe the largest market. These developments have become possible by significant break-throughs in such areas as liquefaction, tanker design, development of insulation materials, and production of storage container materials which do not become brittle at low temperatures. Economic data and costs indicate that hydrocarbon consuming industries can now be located at points quite distant from the raw material source without being limited to pipe-line transport like most petrochemical complexes in the past.

10. This interlink of the hydrocarbon producing and hydrocarbon consuming petrochemical facilities provides a possibility of co-operation between developing countries to achieve a more economical overall pattern of production. Countries favoured with an abundance of raw materials could produce ethylene from large scale cracking installations based on various hydrocarbon feed stocks. Such plants could supply not only local internal requirements, but also ship ethylene to various other points of consumption, particularly to countries where limited market requirements preclude installation of ethylene

producing facilities. Transportation costs, including direct costs plus capital charges, which have been developed recently indicate that quantities from 10,000 to 50,000 metric tons of ethylene annually could be economically shipped over one way distances ranging from 1,000 to 5,000 nautical miles. This development has added impetus to develop the transportation of liquified propylene, and vinyl chloride which could be shipped in essentially the same type of refrigerated tanker as used for the transportation of liquefied natural gas.

2. Intermediates

(i) Olefins

11. Ethylene is the olefin of major importance in the petrochemical industry today. Its availability on a large scale and its low cost has led to the development of a family of major petrochemicals. The demand for ethylene in the U.S. in 1964 was in the neighbourhood of eight billion pounds. It is projected that by 1970 producers will have to add about 1/3 more capacity to satisfy the increasing demand of this raw material. The most important advance in ethylene manufacture with regard to developing countries is the use of high severity cracking of naphtha feed stocks. In industrialised countries, particularly in the U.S.A., most producers manufacture ethylene by ethans and propane cracking. This is not the case, however, in most countries outside the U. S. Naphtha feed stocks is the raw material for 85% of the ethylene produced outside of the U. S. Naphtha feed stocks have a tendency to coke if cracked and severely as ethane and propane. Consequently, most ethylene plants utilising conventional naphtha cracking are limited to 20-25% ethylene yields and produce simultaneously considerable quantities of propylene and four carbon by-products. The new high severity processes for cracking naphtha feed stocks yield more than 30% ethylene. It should be readily apparent that this development is the important innovation in ethylene manufacture to come for sometime; an innovation which is likely to become the standard practice in the next generation of ethylene plants to be built outside the U.S. High severity cracking reduces the overall capital

investment and 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 during the cracking process. The achievement of this is due to the careful control of the time and temperature relationship involved in the cracking reaction. For this purpose the process uses a radically new design in the high severity cracking furnace. It allows careful control 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 feed stock in the furnace.

12. A mixture of feed naphtha and primary steam is fed through an injection tube which extends 7 1/2' down into a vertical 30' long furnace tube. Secondary steam is fed into a furnace tube around the injection tube so that a sheering effect is achieved of the spray at the injection end. Some 2.75' 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 an 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 with oil.

13. It is estimated in petrochemical circles that the high severity cracking furnaces are somewhat more expensive than conventional furnaces for naphtha feed stock. In addition, the quick quench needed with high severity cracking adds to the cost of the furnace effluent-handling equipment. However, both these costs are offset by the reduced distillation costs that result from the smaller amounts of propylene, propane, butylene and butane by-products that have to be separated either for outside consumption or for recycle.1/ An important feature of the high severity cracking is the fact that lighter by-products disappear by recycle and cracking. However, benzene does not crack even under severe conditions. It may be possible, thus, that

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1/ Thus, the cost of the furnace is only 10 - 12% of the total cost of an ethylene plant, while the total installed cost of the entire cracking and quenching section of the ethylene plant is some 25% of the total investment.

high severity cracking of ethylene could be made to compete with reforming as a source for aromatics in developing countries where no reforming facilities have been installed or are planned separately.

(ii) Butadiene

14. In the group of diolefin intermediates the most important members are Butadiene and Isoprene because of their utilization in the production of synthetic elastomers. When synthetic rubber was first developed during World War II, butadiene was manufactured from ethyl alcohol. This process has been abolished in most industrialized countries because it could not compete economically with more recent processes. The present technological practices for theproduction of butadiene are based on dehydrogenation of normal butanes or butenes. Dehydrogenation of butene was also developed in the forties, however, since the early fifties approximately a hundredfold expansion in production facilities for butadiene has occurred in most industrialized countries. This spurred efforts for more economical processes in butadiene manufacture. The most advanced process in this respect is the dehydrogenation of normal butane, as there is a significant price differential in butane and butene feed stocks. As the situation is at present, about 55% of the butadiene manufactured is based on dehydrogenation of normal butene and the remainder under newer processes based on butane dehydrogenation. The latter reaction utilizes 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 by taking advantage of the principle of heat storage in a fixed bed of catalyst and inert particles. It is most likely that facilities for the production of butadiene in developing countries would be established on the basis of the most recent technology - dehydrogenation of normal butane, which is also the least expensive feed stock.

(iii) Isoprene

15. Interest in isoprene is greatly stimulated by the discovery in recent years of all "cis" rubber and its production on a commercial scale. The production facilities for isoprene established ten or more years ago are based on the dehydrogenation of C.5 olefins present in cracked gasoline

fractions. These were plants constructed primarily for the manufacture of butadiene from butenes. Wherever it has been necessary to construct new facilities for production of isoprene in the absence of any existing facilities, as is likely to be the case in most developing countries, several new processes appear to offer definite advantages:

16. 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 opportunity it offers to 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 butadiene-polybutadiene complex is claimed to be 20% higher than that of a comparably sized isoprene-polyisoprene complex using the aforementioned process for isoprene manufacture.

17. 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. Isoprene is produced in this process from isobutylene and formaldehyde. The process is based on the reaction of C_4 refinery streams containing 10-20% iso-butylene, with formaldehyde. The condensation reaction produces a dioxane derivative which is decomposed to isoprene, formaldehyde, one of the initial materials which can be re-cycled, and water. The isoprene so obtained is very high purity and thus the necessity for capital investment in purification and fractionation equipment is reduced.

18. Certain developments make it worthwhile to consider the process for isoprene developed by Societa Nationale Metandotti (SNAM) of the ENI group in Italy. This process is based on the reaction of acetone with acetylene to give methyl butynol. The latter is selectively hydrogenated to methylbutenol (MBE) and then dehydrated to give isoprene. 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 cumene 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 in industrialized countries to less than 5 cents per pound. 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.

19. Before leaving the subject of diolefins, it is worthwhile mentioning some new technology 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 produced 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 a monomer in the production of nylon 66.

(iv) Acetylene

20. Acetylene competes with ethylene as a starting 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. 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 economic 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.F.-Kellog Process which is similar to it, have been mentioned 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.

21. A new process for acetylene already referred to in the preceding papers has been announced. It is claimed that it will 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 eliminates the need for any vacuum pumping equipment and

related problems of seals, maintenance and additional power requirements. A further advantage is that the purification of the acetylene is simple. Raw gases contain no water or carbon oxides 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, U. S. A.) 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.

(v) Aromatic Compounds

22. Aromatic hydrocarbons are intermediates of major importance in the petrochemical industry. Their potential 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 gasolines and other fractions. Recovery is impracticable immediately after this step, as the concentration of naturally occurring aromatics is too low. Straight run gasoline is then subjected to the reforming process. This is a combination of three reactions: cyclisation, dehydrogenation or aromatization, and isomerization or dealkylation. The aromaticity of straight run gasoline varies from less than 5% to about 20%, 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%. This enables the separation of the aromatics and their utilization for chemicals.

23. 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 gasoline 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).

24. A recent development takes a C_8 concentrate from catalytic reforming and Udex extraction containing between 25% and 30% of ethyl benzene and subjects is 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 benzene suitable for styrene manufacture is thus achieved.

25. An important problem for the petrochemical industry in industrialized countries has arisen with the inbalance between the proportions in which the non-nuclear aromatics (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:

	Market	Petroleum	Coal Tar
Benzene	65	10	80
Toluene	20	40	15
Xylene	15	50	5
Total	100	100	100

26. Coal tar aromatic production, however, is intimately linked to steel production. 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 1961-1962, of the total United States capacity for aromatics, 79% of the benzene, 91% of the toluene and 97% of the xylenes were derived from petroleum.

27. To meet the rising demands for benzene without producing additional quantities of toluene and xylene, a process known as hydrodealkylation was commercialized in 1961. 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 hydrodealkylation can also be used. The product stream is stripped to remove methane and excess hydrogen and then fractionated to separate benzene from unreacted toluene.

28. The principal products of hydro-dealkylation are benzene from toluene and naphthalene from alpha-methyl and dimethyl naphthalene. In some naphthalen processes, a high octane gasoline rather than benzene is taken as a by-product. Until the development of the hydro-dealkylation process, the economics for recovering naphthalene from petroleum fractions were not favourable and supplies of naphthalene from coal tar sources were usually adequate.

29. The economic situation which has developed in the supply and demand picture of aromatics in the United States is 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 delakylation 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. 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 up-shot 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.

30. In summing up, whereas there are some doubts as to the importance of hydro-dealkylation for the purpose of benzene production in developing countries, 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 considered 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 important 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 when naphthalene from petroleum was ever considered. It is perhaps worthwhile to note the figures which indicate the vigour with which the petroleum industry 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 in the United States.

3. Chemical End Products from Petroleum and Natural Gas

(i) Fertilizers

31. Some recent developments in the manufacture of ammonia merit special attention by developing countries, and will be described briefly.

32. 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 appropiate compression and a heating cycle, the mixture is circulated around a synthesis loop. It repeatedly passes through a converter containing catalysts to produce ammonia.

33. 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 ton 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.

34. Significant improvements and innovations in the design of the ammonia synthesis converter are due to the J. S. Pritchard Company of Kansas City, Missouri. 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 ton 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.

35. Synthetic ammonia is the main intermediate in the manufacture of the various nitrogenous fertilizers. Ammonia plants constitute the largest item of capital investment in the manufacture of nitrogenous fertilizers. It is important therefore to examine carefully the various factors involved in the manufacture of anhydrous ammonia as the prime building block of nitrogenous fertilizer industry in developing countries.

36. The factors influencing the manufacturing cost of ammonia are largely local in nature. The major items among these are the cost of raw materials, which could account for 25% to 50% of the total cost, depending upon the kind of raw material and its price. Commercially ammonia is produced by direct combination of hydrogen and nitrogen at high pressures and temperatures, with the aid of a catalyst. The nitrogen required in ammonia synthesis is obtained from the air. The two main sources of hydrogen are the hydrocarbons and the hydrogen obtained by electrolysis. At the present time, the greater portion of the hydrogen for ammonia synthesis is obtained by reacting hydrocarbons with steam, oxygen, or mixtures of the two substances.

37. Two methods are presently available for the production of hydrogen from petroleum hydrocarbons. One of these is non-catalytic, the other is the catalytic partial oxidation of both gaseous or liquid hydrocarbon as feedstock. Another method is catalytic steam reforming. Due to the recent development of special catalysts for this purpose, the use of naphtha in the steam reforming process has been made possible. The by-product hydrogen from catalytic reforming is used in the manufacture of ammonia. However, with the development of hydrogen treating processes in petroleum refining, there has arisen an increased demand for this by-product hydrogen for other purposes than ammonia production.

38. In connection with the size of plants, two trends are noticeable in ammonia synthesis plant design at the present time. One of these is the design of large plants ranging in size up to 1,200 tons per day capacity. The other trend is toward the design and construction of relatively small pre-fabricated or "package" ammonia plants mentioned previously. Such a plant, with a capacity of 60 or 100 tons per day, consists of a number of different assembled units, that can be transported to the plant site, connected together and put into operation in a short time.

39. A large plant requires a lower investment per ton of product hence lower assistance charges, plant depreciation, and insurance. The manufacturing costs are substantially lower for the case of large plant sizes. New technological features introduced in large scale ammonia plants include, inter alia, the use of new type of compressors and the application of the "total energy" concept, according to which natural gas is utilized as the raw material and process fuel for the synthesis ammonia. Natural gas is also applied as the source of energy for generating electrical power and to provide the necessary shaft horsepower for compression. It is claimed that costs might vary from $33.25 per ton of ammonia for a 200 ton per day plant down to $26.63 per ton in the case of the 1,000 ton per day plant. It should be noted that the availability of a large ammonia market and low-cost transportation to this market are of particular importance to a high-capacity plant.

40. Sometimes because of the geographical conditions within a particular country, the cost of transport can rise to an uneconomic level. In this case, a small unit will be economical. A small unit permits a developing country to enter this field with a much lower initial investment for covering its fertilizer demands.

(ii) Plastics

41. Plastics 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 unlimited numbers of ways that they can be formulated and the almost inexhaustible supply of their raw materials, have contributed to their ever-growing demand all round the world, replacing traditional materials and fulfilling new needs.

42. At the present time, the amount of production and consumption of plastics has surpassed that of the basic non-ferrous metals such as zinc, copper and aluminium and as a group, they represent the biggest outlet of the petrochemical industry after nitrogenous fertilizers.

43. In the developing countries, plastic materials have already found multiple end-uses, particularly in the form of consumer goods and, to a limited extent, as compound parts of other goods, as construction materials and in packaging.

44. In most cases, the plastic processing industries of the developing countries, must import the petroleum-based resins they use as raw materials from the more industrialised countries, which implies the expenditure of important amounts of foreign exchange on the part of developing nations. As a result, some important industrial and construction applications of plastics have not yet been developed in these countries.

45. The actual rate of growth of this industry is dependent upon the availability of raw materials, by-products utilisation and the ability to produce plastics at a low price. With the setting up of petroleum refineries, naphtha for petro-chemical use is expected to be available in adequate quantities. Prices are also expected to fall as a result of gradual and profitable utilisation of by-products. This will simultaneously require special efforts in setting up of units to process plastics into end products and to supply plasticizers/chemicals required for this purpose.

46. The major types of plastics of interest for developing countries are:

(a) Polyolefins : high and low density polyethylenes, polypropylene;
(b) Vinyls : polyvinyl chloride;
(c) Styrenes : polystyrene and copolymers;
(d) Engineering plastics : Nylon.

(a) Polyethylene

47. Discovered 30 years ago, low-density polyethylene has established one of industry's most astonishing growth records.

48. In the packaging field, polyethylene has made possible unbreakable bottles, liquid-holding paper cartons, no-dent cans and moisture-proof shipping bags - concepts that were not even in the idea stage at the time polyethylene was discovered.

49. In 1963, the countries outside centrally planned economies used 1,350,000 metric tons of low-density polyethylene. By 1970, this amount is expected to almost triple.

50. Single biggest use of low-density polyethylene is flexible film and sheeting, most of which goes into packaging. Other major uses are injection moulding, extrusion coating, wire and cable, pipe and blow-moulding. The newer larger volume applications are as follows: bread-wrap film, shipping bags, extrusion-coated milk and frozen-food cartons, agricultural mulch and insulation for submarine and telephone exchange cable.

51. The most suitable process for polyethylene manufacture in developing countries, may be the utilisation of high pressures technology because of the established process know-how and greater demand for high pressure polyethylene. Despite increasing competition from high-density polyethylene and polypropylene, low-density polyethylene is closing in on poly-vinyl chloride as world's most widely used plastic.

(b) Polyvinyl chloride

52. 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. Polyvinyl chloride's array of properties include excellent water resistance, chemical resistance, good strength, abrasion resistance and ease of colouring. When compounded with plasticizers, finished products with nearly any degree of flexibility can be produced.

53. The raw materials needed for vinyl chloride are acetylene or ethylene and chlorine or hydrogen chloride. The basic routes to vinyl chloride are: (1) addition of hydrogen chloride to acetylene, (2) direct chlorination to

dichloroethane, (3) oxychlorination of ethylene followed by cracking. Two process variations are: (i) combined facilities-chlorination of ethylene plus hydrochlorination of acetylene and (ii) combined hydrochlorination and chlorination utilising a dilute acetylene and ethylene feed.

54. The acetylene route has the advantage of lowest capital investment; the direct chlorination of ethylene followed by cracking of dichloro-ethane, offers lower raw material costs; the newer oxychlorination process will be of considerable importance because it combines use of cheaper ethylene with elimination of by-product hydrogen chloride. The combination routes combine advantages of the various routes for special applications.

55. Recently another process for the manufacture of vinyl chloride has reached industrial status. The process was developed for the exclusive production of vinyl chloride without the need of a multi-million dollar petrochemical complex and is believed to be the most economical vinyl chloride process. The process is advantageously used to produce low cost vinyl chloride where carbide acetylene and ethylene are not economically available:

56. The process consists of a combination of the following steps.

(a) High temperature naphtha cracking which produces cracked gas containing acetylene and ethylene.

(b) Vinyl chloride synthesis by reaction of cracked gas containing acetylene with hydrogen chloride.

(c) Ethylene dichloride synthesis by reaction of chlorine with cracked gas containing ethylene.

(d) Thermal cracking of ethylene dichloride to vinyl chloride, and separation of hydrogen chloride for reaction in the above step.

(e) Separation and purification of vinyl chloride obtained in the above steps to obtain high purity monomer.

57. Of the three polymerization routes, solution, bulk and suspension, the suspension polymerization technique offers the lowest capital investment and the lowest production costs. This process also lends itself readily to the production of copolymers which are used for special applications.

58. Because the suspension process for producing polyvinyl chloride is a batch process, it is possible for relatively small plants to compete with large installations. As in vinyl chloride production, the main factor in polyvinyl chloride production cost is the raw material-vinyl chloride.

(c) Polystyrene and Copolymers

59. World-wide production of styrene resins, accounted for by some 40 countries, is expected to reach 2.5 million metric tons by 1970. The broad acceptance of these resins can be ascribed principally to low cost, processing ease, excellent transparency, and availability in an unlimited range of attractive colours.

60. In the main, the styrene 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.

61. Commercial properties of each of these grades are determined, above all, by molecular weight, residual monomer content, and additives. General-purpose resin is a true homopolymer of styrene. High-impact polystyrenes are produced by incorporating rubber -usually SBR- into the polymer. Originally, this was done by mechanical blending, but the bulk of today's impact polystyrene is made by graft-polymerizing styrene onto a rubber base.

62. Acrylonitrile-butadiene-styrene copolymers (ABS) are thermo-plastic polymers produced by either blending styrene-acrylonitrile resins with butadiene-based elastomers or by grafting styrene and acrylonitrile onto polybutadiene. Although sometimes classified as a special kind of high-impact polystyrene, acrylonitrile-butadiene-styrene copolymers are generally considered as a class by themselves. They exhibit an extraordinarily desirable combination of mechanical, thermal, chemical and electrical properties as well as ease of processing and a moderate price.

63. As engineering plastics they can be classified with nylon resins, polyformaldehyde acetal resins and polycarbonates. They are used where high performance but a relatively low cost is desired. Typical outlets are telephones, pipes, household appliance, automobile parts, luggage, shoe heels and packaging.

64. The fabrication of end products from ABS plastics is easy as these plastics can be injection moulded, extruded to sheets and pipes, vacuum formed, calendered, machined, embossed, lacquered, enamelled, printed, metalised and bonded to metal and wood. Cast films or coating can be obtained by spraying or brushing from solvents such as diacetone alcohol. A feature important for their application as pipe is the ability to be "solvent welded".

65. Besides the three principal types of general-purpose plastics already discussed, there exist several other types of plastics materials developed for specific applications. These resins are grouped under the generic name of "engineering plastics". The important representative of this family is nylon.

(d) Engineering Plastics

66. Nylon is a generic term for polyamide resins. Resins of this type can be formed by condensation polymerization of a dicarboxylic acid and a diamine (nylons 66 and 610) and by the polycondensation of lactams (nylon 6 and 12). While the chemical structures and physical properties of the two broad types of nylon are similar, they are not identical.

67. Nylon monomers are adipic acid and hexamethylenediamine for nylon 66 and caprolactam for nylon 6. 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 benzine although some is obtained from refinery streams. Hexamethylene-diamine may be produced by the hydrogenation of adiponitrile over a supported-cobalt catalyst. The

adiponitrile is produced from adipic acid by way of its ammonium salt and also from butadiene. 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 hexamethylene-diamine by reductive ammination.

68. Industrial processes for the production of caprolactam are based on cyclohexane, phenol or toluene. The most widely used processes convert cyclohexanone to its oxime by treatment with hydroxylamine sulphate. The oxime is converted to caprolactam by a Beckman rearrangement.

69. The polymerization of hexamethylenediamine and adipic acid to produce nylon 66 is a relatively simple process. In the production of nylon 6, caprolactam is first converted to the corresponding "omega" amino acid by water and the "omega" amino acid is then condensed at an elevated temperature. Reduction of monomer and low molecular weight polymer content in polycaprolactam is one of the most serious problems in the production of nylon 6.

70. Of importance to developing countries is to note that nylon 6 production requires less capital investment and nylon 6 fibres are easier to spin. Nylon 6 is also believed to be less costly to produce. In addition all processes for the production of caprolactam which have cyclohexanone as an intermediate will produce ammonium sulphate as a by-product, which can be used for fertilizer.

71. The establishment of a plastics industry in a developing country often leads to the use of plastic materials in the construction industry. Plastics have advantages over a number of conventional materials in freedom from corrosion, resistance to rot and decay, ease of handling, low density and low-skill levels required for installation. Available plastics -both thermoplastics and thermosets provide a versatility and range of properties fitting many construction needs, ranging from paints and coatings to flooring,

wall panels, piping, roofing, insulation and structural members. Present building used account for 22 to 25 per cent of all plastics produced in the United States and Europe.

72. To this state of technology may be added a number of factors that promise a bright future for plastics in meeting the construction needs of developing countries. Present unfilled housing requirements and the volume of future demands far exceed those in developed nations. Petroleum as a raw material is available in many cases where the need is the most serious and the shortage of wood and metals is the greatest. Large-volume production of plastics from the naphtha fraction of petroleum is compatible with refinery product balances in developing countries and with the general development of a petrochemicals industry in these areas. The well-proved variety and versatility of plastics can go far to fill the void left by the shortage of conventional materials of construction. Pioneering studies have demonstrated certain aspects of the feasibility of plastics in meeting the special construction needs of these countries. Future specific applications based on present technology may lead readily to wall materials, roofing structures, windows, doors, water supply, and sanitary facilities - as well as all plastics houses built on a flexible modular design.

(iii) Synthetic Elastomers

73. Until the beginning of World War II, natural rubber was the predominant elastomer in commercial use. However, since the war period synthetic rubber has been steadily gaining an increasing share of the total rubber market. This is due, inter-alia, to improvement in the quality of SBR, (styrene-butadiene rubber), cost reduction as well as the production of various types of rubber other than SBR, with specialised properties. Production of synthetic rubber has grown at a faster rate (11% per annum since 1950) than natural rubber (about 1%). By 1962, the share of synthetic in total rubber production exceeded that of natural rubber.

74. Synthetic rubbers include, styrene-butadiene copolymers, chloroprene, butyl, nitrile, polysulphide, silicone, chlorosulphonated polyethylene, as well as the stereo-regular rubbers, i.e. "cis"-polybutadiene, "cis"-polyisoprene, and ethylene-propylene copolymers and terpolymers.

75. SBR accounts for about 70% of total synthetics. It is a versatile rubber, the oil-extended varieties of which are the cheapest rubber available. Oil-extended SBR is satisfactory for use in passenger car tyres. Butyl, chloroprene, and nitrile rubbers have established markets as specialty rubbers. Butyl rubber is relatively impermeable to air and has good resistance to heat and oxygen. Virtually all inner tubes in the United States and Europe are made from butyl rubber.

76. The high resilience and low heat build-up of the vulcanised polyisoprene rubber are among the qualities which make it a good substitute for natural rubber. In addition, it is easy to process, and it can be used in the formulation and recipe in conventional rubber processing equipment.

77. Polybutadiene rubber has superior qualities over SBR in that it has improved wear, heat build-up and groove crack resistance when used in treads of passenger-car tyres. Its disadvantages are low resistance to chipping and difficulty in processing. In order to overcome these difficulties, polybutadiene is being used in 1:1 blends with natural rubber in heavy-duty tyres, and in 1:3 blends with SBR in passenger car tyres.

78. The properties of ethylene-propylene capolymers (EPR) at first sight appear to be similar to those of SBR but it has in addition a remarkable resistance to ageing and ozone attack. It has been known that EPR is difficult to vulcanize. However, by including an unsaturated diene, vulcanizing has been carried out in the conventional way using sulphur.

(iv) <u>Synthetic Fibres</u>

79. At the present time, approximately 25% of the total fibre demand in the United States and Western Europe is met by man-made fibres of which 25% are of

fully synthetic origin (50% polyamides, 20% polyesters, 17% acrylics, 13% others). In 1963 the production of synthetic fibres exceeded 1.3 million tons and the annual growth rate is more than 20%. In the industrially advanced countries the average per capita consumption ranges between 1-2 kg. per year, compared to an average world consumption of 0.3 kg. per year.

(a) Polyamides (Nylon)

80. With respect to types of synthetic fibres currently in use, polyamides (nylon) is the most predominant fibre followed by acrylics and polyesters. Two varieties of nylon, namely nylon 6 and nylon 66 are now being produced in large quantities. They are essentially indistinguishable by the consumer. It is generally conceded that nylon 6 production requires less capital investment and nylon 6 fibres are easier to spin. Nylon 6 is also, in general, less costly to produce. A large number of different processes are available for caprolactam (nylon 6 monomer) production. There does not seem to be any one definite process having absolute superiority over others, and there will generally be one process best suited to the raw material and by-product situation of each particular developing country.

81. Caprolactam may be produced from cyclohexane, benzene or toluene and phenol as primary raw materials. In the case of cyclohexane and benzene, the routes of synthesis are via cyclohexanone oxime and the synthesis of this intermediate is the key to the manufacture of caprolactam. Six processes are now employed industrially for the production of cyclohexanone oxime. Two of these processes go by way of cyclohexanone which in turn is produced either by dehydrogenation of cyclohexanol obtained from phenol or from the mixture of cyclohexanol and cyclohexanone obtained by oxidation of cyclohexane. The oxime can be synthesized directly from cyclohexane by treatment with nitrosyl chloride (photo-chemical nitrosation) or indirectly through nitration of cyclohexane followed by catalytic reduction of the nitrocyclohexane. When toluene is the raw material it is oxidized to benzoic acid which

is reduced to cyclohexane carboxylic acid. Treatment of this acid with nitrosylsulfuric acid yields caprolactam directly although cyclohexane oxime is probably an intermediate.

82. As already mentioned there is no general agreement as to which process for the production of caprolactam is most suited for a developing country. The various methods for preparing caprolactam, and the side-processes linked with them, show many points of resemblance. In all processes a hydrogenation has to be carried out in some stage of the process and in all processes ammonia is needed. The ammonia is employed as starting material in the preparation of auxiliary materials (NH_2OH, $NOCL$, HNO_3) and for neutralization of the sulphuric acid used.

83. The choice of the process will depend for the greater part, on factors such as production capacity, raw material position, special demands as to the amount of by-products, etc. The quality of the end products may well be a decisive factor. All of the processes for the production of caprolactam which have cyclohexanone oxime as an intermediate produce ammonium sulphate as by-product. This may be desirable in a developing country because of the use of ammonium sulphate as a fertilizer. For profitable manufacture of filaments and fibres, the following lowest capacity limits for nylon plants are stated: filament from nylon 6 chips, the minimum daily capacity is held to be 1000 kg. - from caprolactam the figure is estimated at 1500 kg. per day and for staple fibre from caprolactam at 2000 kg. per day.

84. However, the lower capacity limits cannot be taken as a basis if it is intended to export nylon fibres. In this case, the same standards hold good for the design of a nylon filament plant as those existing in an industrially developed country unless the export is subsidized by the government. It is stated that there are opportunities for export to the world market only in the case of a plant of at least 3000 kg. production per day. Comparison of the production cost for plants of different sizes shows that for small size plants polymerization of caprolactam is not profitable.

(b) Polyesters

85. Polyesters now in commercial production for fibre manufacture consist almost exclusively of polyethylene glycol terephthalate (dacron or terylene). This polymer is formed from the basic monomers or from dimethyl terephthalate and ethylene glycol or ethylene oxide. Such terephthalate fibres differ from polyamide fibres mainly in respect to their elastic properties, and have been accepted primarily for clothing purposes. Polyester fibres are also characterized by their low water absorption; the poor dye affinity of polyester fibres is due to the low water absorption, the low swelling tendency and the high crystallinity of the stretched fibre. Polyesters also have a tendency to pile in clothing.

86. Terephthalic acid is produced by oxidation of p-xylene or by the Henkel process which involves the re-arrangement of the potassium salt of benzoic acid or o-phthalic acid. The oxidation of p-xylene to terephthalic acid may be by nitric acid or by air. Essentially all new plant capacity based on p-xylene oxidation has been installed using air oxidation techniques. The Henkel process is held to produce a very pure terephthalic acid which eliminates the necessity of purification via the dimethylester. The smallest economical size plant for the production of terephthalic acid from o-xylene by the Henkel process is stated to be 6,000 tons per year.

87. Ethylene glycol comprises less than one-half of the weight of the polymer in a polyester fibre, and therefore, very large fibre manufacturing operations would have to be undertaken to require a glycol supply that would be produced in an economic sized plant. The decision of a developing country to make or import ethylene oxide or ethylene glycol would depend on the possibility of other uses for ethylene glycol.

(c) Acrylics

88. Most of the synthetic fibres based on acrylonitrile are produced from copolymers for the purpose of improving the properties of the fibre. Such

fibres spun from copolymers are classified into fibres whose acrylonitrile content is 85% or more (acrylic fibres) and fibres whose acrylonitrile content is less than 85% (modacrylic fibres).

89. At the present time, most of the acrylonitrile is produced from acetylene and hydrogen cyanide. An alternative route, in which propylene and ammonia serve as raw materials, is becoming important in the production of acrylonitrile. This process has the following advantages: lower cost and lower investment, greater potential abundance of suitable raw materials, process simplicity, lack of the necessity to handle hydrogen cyanide and high end-product quality.

4. New Transportation Techniques

90. A recent development of major importance to developing countries which was mentioned previously, involves transport of liquid ammonia and ethylene produced in large capacity units. In Trinidad a unit for production of anhydrous ammonia has already been set up with a capacity for production of the order of 230,000 tons and soon this capacity will be raised to 500,000 tons of ammonia per year. This large unit is being set up in order to first produce ammonia at a very low price and then export it in tankers. The ammonia is stored in the tankers at atmospheric pressure and a temperature of minus 28°F. Special ships as well as receiving terminals in the importing countries are provided to ensure that individual shipments of 9,000 tons of ammonia can be made. This system may assist the developing countries to produce nitrogen fertilizers in a shorter time by importing ammonia and then either using it as ammonia or in the form of fertilizer compounds. The position is similar with respect to transport of liquid ethylene. It is estimated that the transport cost of liquid ethylene decreases considerably when the total amount of ethylene transported to a single point every year increases from 10,000 to 50,000 a year. At the latter figure the cost of handling per ton of ethylene is as low as $4 per ton. It is apparent that where the requirement of

ethylene is large it would be more satisfactory to produce such ethylene in a naphtha cracker and where the requirement in a developing country is for smaller amounts of ethylene in the initial stages it might be useful for such countries to import liquid ethylene.

5. The Problems of Technological Obsolescence and Developing Countries

91. An important factor when establishing Petrochemical Industries in developing countries is to guard against acquiring already obsolescent technological processes from industrialised countries. Although on the face of it such processes may sometime be available at very low initial costs, the installation of obsolete technology is fraught with danger. It places a developing country very soon at a distinct economic disadvantage; i.e. the inability to compete on regional or international markets with the petrochemical products produced. Bearing in mind that the local market in most developing countries is limited, this brings about a situation where a substantial capital investment has been made and often the products are made at a unit price exceeding that available on the international market. A specific example in this regard is the use of ethyl alcohol for the production of butadiene and SBR rubber in two developing countries. The use of calcium carbide for acetylic - vinyl chloride manufacture, often suffers from similar disadvantages.

III. Chemicals from Petroleum - Industrial Developments in Developing Countries

1. Distribution of Petrochemical Plants

92. Of the approximately 1,000 petrochemical plants in existence more than 50 per cent are located in the United States and Canada, about 200 in Western Europe, some 50 in Japan, the rest being distributed among all other areas. Nevertheless, now projects or plants in construction were at the end of 1963 distributed more evenly among the United States, Western Europe, Japan and developing areas. Table 1 shows the world-wide distribution of petrochemical plants and projects.

Table 1

World-Wide Distribution of Petrochemical Plants in 1963

Country	Existing Plants (1)	Projected or under Construction (2)	Ratio of Projected to Existing Plants (1) : (2)
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[a]	82	72	0.88
Total	933	255	0.27

a/ Centrally planned economies not included.

93. Among developing countries there has been, in recent years, increased investment activity in the petrochemical field. Table 2 summarises data available for recent years on existing petrochemical plants and projects in developing countries.

Table 2

Petrochemical Plants and Projects in Developing Countries - 1961, 1962, 1963

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

94. Up to last year the majority of the existing plants and projects in developing countries was still concentrated in Latin America and Asia, which accounted for 90 per cent of the total. 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 and the Far East, India had the majority of the installed and projected plants.

95. This information is, of course, just 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 1/3 of the total, plants of the production of elastomers and fibres accounted only for about 8 per cent of the total number.

Table 3

Petrochemical Plants and Projects in Developing Countries, Classified by Products Line - 1964

Product	Plants	Percent
Ammonia and nitrogenous fertilizers	41	32.4
Plastics	30	24.0
Synthetic Rubber	7	5.5
Synthetic Fibres	3	2.4
Others *	42	33.3
Unspecified	3	2.4

* Includes: Acetone, carbon black, sulphur, benzene, toluene solvents, detergents, insecticides, etc.

96. Fertilizer plants rank first, on account of the growing demand for nitrogenous fertilizers to increase food production, 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 their development would imply the substitution of traditional industries sometimes based on domestic raw materials.

97. In order to evaluate the extent of application of the available technology in developing countries one could examine the type of production facilities installed, the end-products, intermediates and raw materials being produced and the processes being used. Although such an evaluation would require detailed data not yet available, an indication of the prevailing trends could be tentatively ascertained from the studies presented at the recently held Petrochemical Conference in Teheran.

98. It follows from it that countries with a sizeable present, or potential, market like Argentina, Brazil, Mexico and India, have initiated vast programmes for the development of petrochemical industries. All these plants or projects utilise imported technology obtained either by licensing, joint ventures or direct foreign investments. Provided that a consistent policy is followed, for the rapid application of modern technology to petrochemical production processes, any of these methods will serve as a vehicle for the transfer of the necessary technological know-how. In this context, it is the industrial development policy followed by a country which will determine to a large extent the quality and modernity of the technology utilised.

2. Product Lines

99. In considering the different petrochemical product lines the following aspects should be emphasized:

(i) Nitrogenous Fertilizers

100. Capacities, feed-stocks and processes used in developing countries are quite diverse. Plants are generally smaller than in the United States for

example. Thus, while there are already large-scale plants for ammonia production in Trinidad and projects are being finalised for even larger plants in Mexico and Kuwait, the average ammonia plant in developing countries is rather small. At the same time there is a trend towards utilising-even in industrialised countries-small-size plants using new technology for the production of ammonia, the main building block in this family of products.

101. Countries rich in oil or natural gas are basing their production of ammonia in these feedstocks, while countries like Brazil and India, for example, have to rely on the cracking of naphthas available from the refining of imported crude oils; this implies the use of different processes and equipment. Because of the high priority assigned to a rapid increase in agricultural productivity in the developing countries, construction of fertilizer plants is widespread and increasing in these countries. Although the plants are not always of optimum size this has to be compared in many cases with the alternative of no fertilizers at all due to severe restrictions on foreign exchange availability. A new possibility which is still in the formative stages is the alternative offered by importing ammonia based on natural gas, and produced in very large installations, like those in Trinidad, and starting domestic manufacture from there on, for countries which do not have an equally competitive position in raw materials and/or a large enough initial market. This alternative can also be utilised in the case of other intermediate feedstocks (such as butadiene, styrene, etc.), due to improvements in cryogenic techniques for ocean shipment of ammonia.

(ii) Plastics

102. In this field the majority of the installation in the developing countries are devoted to the production of polyvinyl-chloride (P.V.C.), polyethylene (low density, high-pressure type) and polystyrene.

103. In most developing countries the installation of plastic processing

industries preceded the production of the plastic resins and raw materials. Producers have been exposed in this way to the utilisation of various molding grade resins and different types of equipment for various uses and final products. Production of polymers is usually initiated when the internal markets are already developed to a certain extent.

104. The production of polyethylene and polystyrene can be jointly organised because they are both based on the same building block: ethylene. In addition, since styrene is also used for the production of styrene-butadiene rubber, the combined demands of these products may justify an ethylene cracker long before the demand originated in, say, only polyethylene, would warrant it. The know-how necessary for the production of polyethylene (low density), although available, is still restricted to just a few American and European producers. This is very much so, also with regard to high density polyethylene since existing patents still restrict the availability of the technology involved.

105. In the case of P.V.C. the existing plants in developing countries are generally based on acetylene obtained from calcium carbide, this also being the pattern followed initially in Europe and Japan. The trend in these areas is now to switch to either ethylene based P.V.C. or to acetylene obtained from natural gas whenever available.

106. The calcium carbide acetylene production, although economically justified in areas where cheap energy is available, is becoming obsolete and this is the reason why there is a distinct trend towards scrapping such installations.

107. Increasing attention is being paid in some developing countries to the possibility offered for the joint production, by the Zeigler-Natta process, of the new type of polyethylene (high density) and polypropylene and eventually other polyolefins. The reasons for this are multiple: The new high density polyethylene will eventually substitute the low density type in many uses; the installations required for high density polyethylene are still smaller (the effect of a recently developed technology) and more flexible, permitting thus the production of various polyolefins in the same plant.

108. Plastics as a group follow nitrogenous fertilizers with regard to output and production installations in the developing countries. Attention is initially generally paid to light molded consumer products, and there is ample room for further expansion of output in the production of heavy and structural type of goods, in which the utilisation of plastics can substitute for metals, glass and wood which are scarce in many of the developing countries. Such products include plastic piping, structural components for housing, floor-tiles, packaging, etc.

(iii) Synthetic Elastomers

109. Production of synthetic rubber is still restricted to only a few of the developing countries. There are still in this field major constraints to the availability of the technology required. As a proof, most of the world production capacity is still concentrated in the United States and only recently have plants been erected in European countries. Nevertheless, a few of the more industrialised of the developing countries, like Brazil and Argentina, have already started the production of the SBR type of synthetic rubber, and plans are being made for new installations in other countries, like for example Mexico and India. Brazil is especially noteworthy among the developing countries because a huge capacity for synthetic rubber production - including also new rubbers like "cis"- polybutadiene is rapidly being built up.

110. The necessary technology and especially the know-how have to be obtained from one of the major commercial producers, although for the new type of rubbers, especially "cis"-polybutadiene and "cis"-polyisoprene, new processes are being developed and could be obtained from process design firms.

111. Since by far the major use of synthetic rubber is for automotive tyres, it is natural that only those developing countries with a substantial demand for tyres will have sufficient demand for the construction of a synthetic rubber plant. This is the case with the countries mentioned above, Brazil and Argentina.

112. The technology for SBR rubber production is well known by now, however, specialised know-how is still required to produce even this conventional type of synthetic rubber. Although it is commonly accepted that the production of SBR requires a minimum economic size of 30-40,000 tons per year, there are apparently no technological reasons for this minimum size constraint, at least in the phase of copolymerisation. Plants recently installed in Europe making use of imported styrene and butadiene do not show such technological indivisibilities in the process of production of SBR to warrant a minimum economic size of above 30,000 tons per year. There are in these plants a plurality of reactors, ovens, etc., which permit one to infer that the minimum economic capacity - from the point of view of investment and production costs without considering extra plant overhead and infra-structure - is well below the aforementioned minimum ceiling.

(iv) Synthetic Fibres

113. As in the case with synthetic elastomers, there are still very few synthetic fibre plants in the developing countries. Although in this case the size constraint is not so operative as in the case of other petrochemically based productions, the technology is still concentrated among a few large commercial fibre producers. The general pattern of development to be found, in those developing countries where synthetic fibres are being manufactured, is one based on backwards integration; i.e. starting from the spinning and polymerization phases with imported monomers and later on going into integrated production including that of the monomer itself. These initial stages of production are less capital intensive, but they do demand a core of skilled labour and operating know-how which is necessary to import from the industrialised countries.

114. It is interesting to mention in this context the Japanese experience. Synthetic fibres are in Japan the largest single sector in the petrochemical output, accounting for a share of more than 20 per cent, while in the United States it is considered to be less than 10 per cent of total petrochemical

output. Part of the explanation to this probably lies in the fact that basic petrochemistry, e.g. the production of intermediates, is far more developed in the United States than in Japan. Nevertheless, it is a structural feature worthwhile to be noticed by the developing countries planning to install petrochemical industries.

115. Among the synthetic fibres being produced or programmed for production in developing countries, the most important are: nylon 66 and more recently also nylon 6, polyester fibres (Dacron, Terylene) and acrylic fibres (Orlon). Latin American countries, for example Argentina, Brazil, Colombia and Mexico, have either started or are in the project phase of the spinning and polymerization stages, and in some cases plans are already being drawn up for the production of caprolactam for nylon.

116. Processes for caprolactam are now available from different sources, including process design firms, and this coincides with a trend towards producing nylon 6 instead of nylon 66 because it requires a simpler technology and less capital investment. Polyester based fibres are also being used in developing countries in different mixtures with cotton textiles, and domestic production in some of these countries is already being planned.

117. Some centrally planned economies have also become recently interested in rapidly acquiring the technology for synthetic fibres production. Commercial arrangements with western countries, including the import of complete plants and long-term financing, are being negotiated.

118. Such example may have to be followed in the near future by some of the developing countries, with a large enough domestic market, and interested in a rapid assimilation of the technology for synthetic fibres.

V. Conclusions

119. The problem for developing countries is, in the long run, to catch up with the industrialised countries on the generation and utilisation of new technology. In the initial stages of industrial development, however, the key question is how to effectively utilise the "best" available technology for each purpose and condition. This approach can be well illustrated by referring to the tremendous growth experience of the Japanese petrochemical industry in a period of less than 10 years, on the basis of imported technology. Mexico provides a similar example.

120. Special skills and know-how are embodied in the three phases of construction of petrochemical facilities: process design, mechanical design and construction. While process design would seldom be available from local sources, many developing countries do have a pool of engineering and technical skills competent enough to undertake locally part of the mechanical design and construction engineering. The same is true for the engineering and industrial facilities required for the production of a major portion of the plant equipment.[1]

121. Some of the major components of the cost of the equipment requirements for petrochemical production consist of relatively simple items, such as piping, valves, storage tanks, and structural steel, which could be produced in many developing countries. At more advanced stages of industrialisation the construction of more sophisticated items of equipment like compressors, pumps and generators, may be added. The co-operation of constructors, licensors, foreign investors and engineering companies is necessary in order to provide

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[1] See: United Nations - ECLA - *The Manufacture of Industrial Machinery and Equipment in Latin America* - 1 - *Basic Equipment in Brazil*. Sales No. 63.II.G.2, New York, 1963; United Nations - ECLA - *The Manufacture of Basic Industrial Equipment in Argentina* - II - *The Production, Transport and Refining of Petroleum and Natural Gas, the Petrochemical Industries* - E.CN.12/629/Add.1, November 1962, and *Programming Data Summary for the Chemical Industry* by T. Vietorisz to be published in the "Industrialisation and Productivity Bulletin" No. 10, Centre for Industrial Development, United Nations, New York

for the possibility of local supply of such equipment. Provisions have to be made during the mechanical design stage to comply to the raw material specifications and construction possibilities in each country.

122. Governmental policy should play a role in stimulating such arrangements. It is important to realise that the early utilisation of domestic skills is a valuable pre-requisite for the formation of the engineers and technicians essential to further petrochemical industrial development. Special attention should be paid to the creation of a modern chemical and mechanical engineering work force which could operate and maintain plants of imported process design, develop specifications for mechanical design using domestic equipment and materials, and eventually deal with adaptations of the technology to local raw materials and operating conditions.

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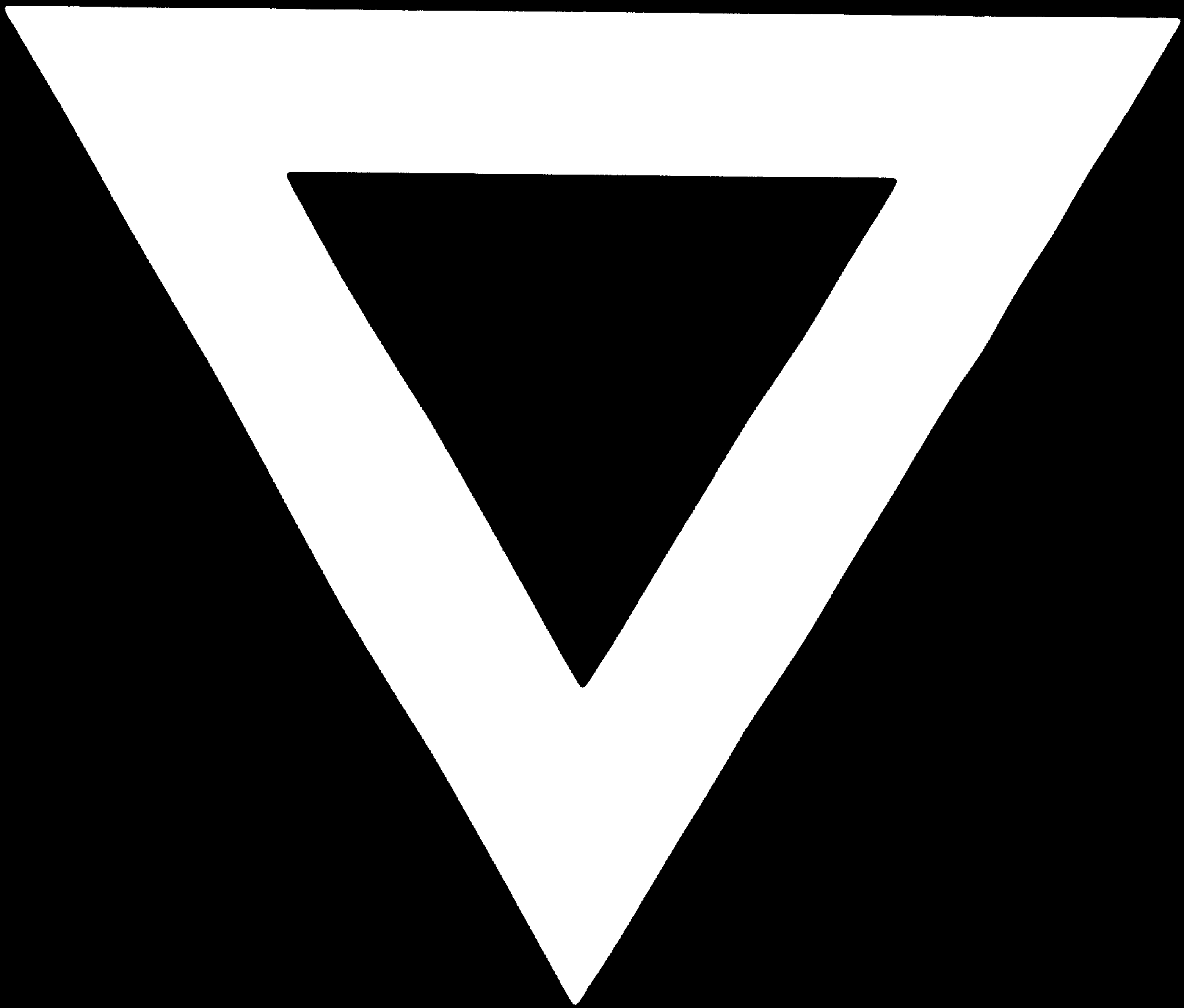

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