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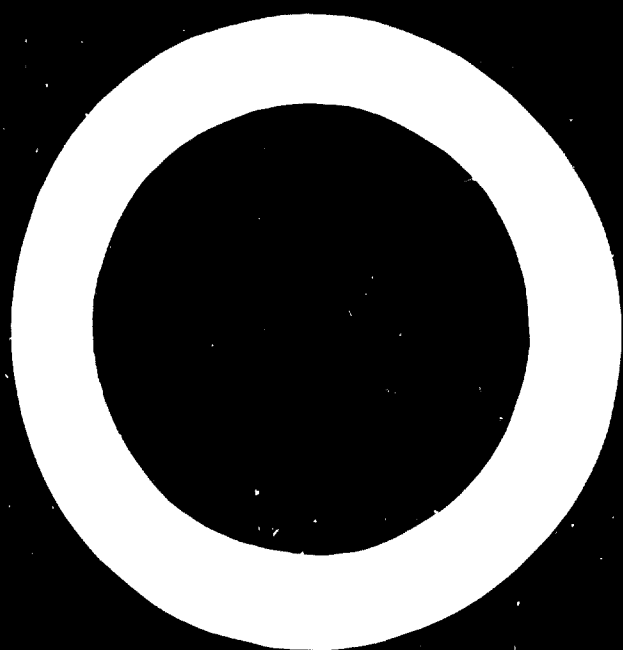
PETROCHEMICAL INDUSTRY SERIES
MONOGRAPH No. 2

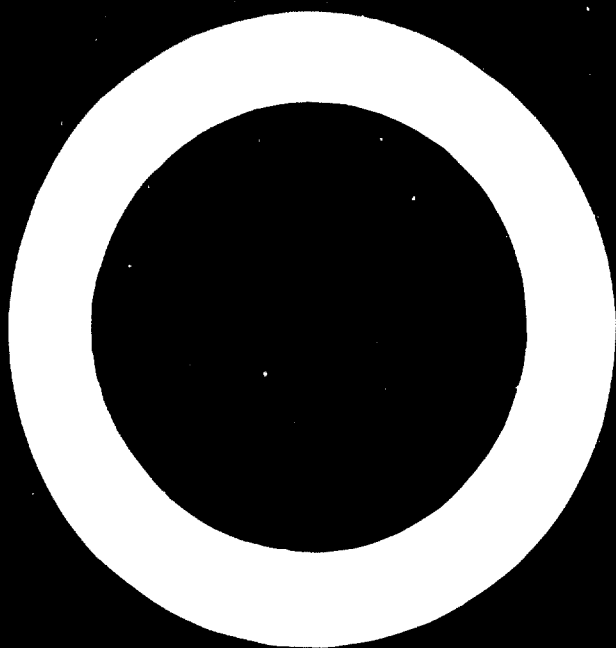
**SELECTION OF PROJECTS
AND
PRODUCTION PROCESSES
FOR BASIC
AND INTERMEDIATE
PETROCHEMICALS
IN
DEVELOPING COUNTRIES**

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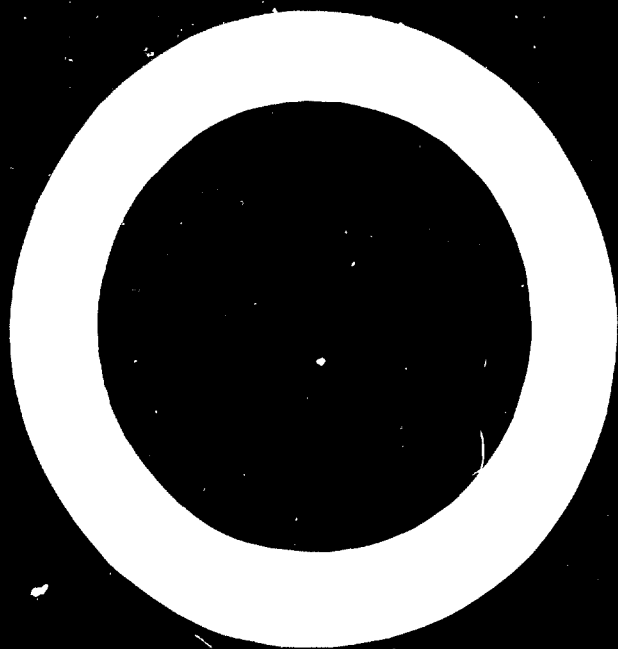


UNITED NATIONS





**SELECTION OF PROJECTS AND PRODUCTION PROCESSES FOR
BASIC AND INTERMEDIATE PETROCHEMICALS IN
DEVELOPING COUNTRIES**



UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION, VIENNA

PETROCHEMICAL INDUSTRY SERIES

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FOREWORD

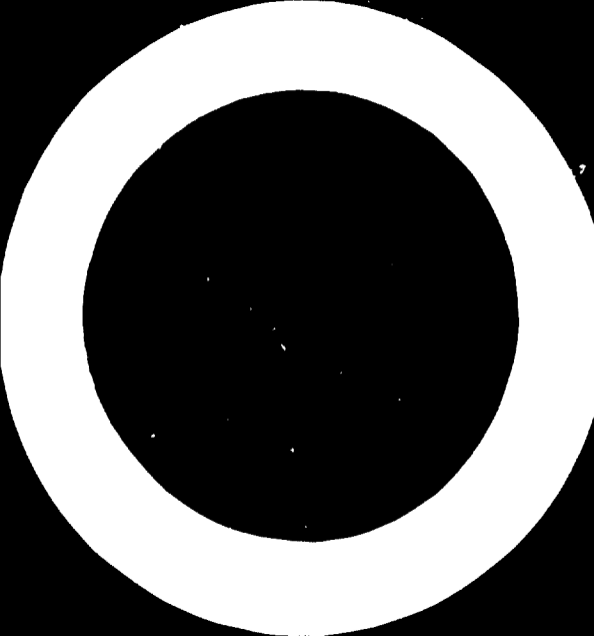
This publication is the second of a series of monographs in the Petrochemical Industry Series to be published by the United Nations Industrial Development Organization. The titles of other studies in this series will be found on the back cover of this publication.

The world petrochemical industry has shown a high rate of growth during the last ten years. The industry supplies intermediate products for a number of other industries and provides substitutes for traditional materials such as steel, lumber, packaging materials, natural fibres, natural rubber and soap. It is considered to be one of the most strategic sectors of industrial development because most of its products go on to other producing sectors.

This series of monographs is designed to assist the developing countries in dealing with technical and economic problems related to the establishment and development of facilities for the manufacture of petrochemicals and consumer products. The present series is concerned with basic and intermediate petrochemicals and end products, such as plastics, synthetic rubbers and synthetic fibres. Nitrogenous fertilizers¹ and textile production based on synthetic fibres are excluded from the series.

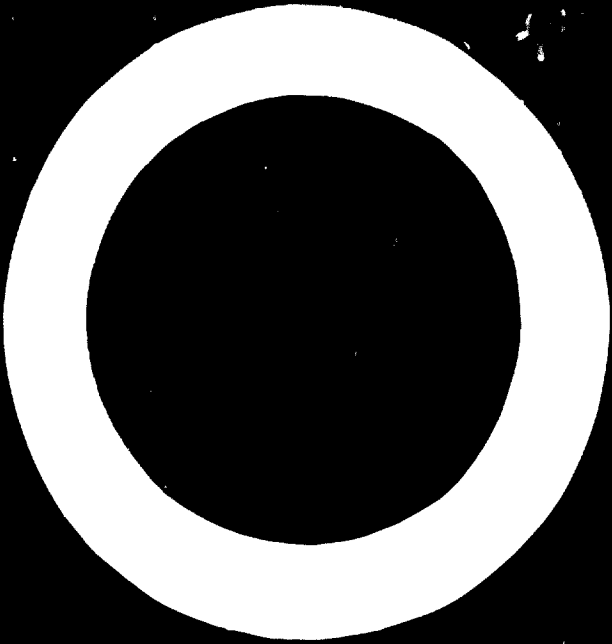
The present paper, prepared by Mr. Alan Benton in his capacity as consultant to UNIDO, reviews the processes for the production of major petrochemicals. It is not intended to be comprehensive, but is written as an initial guide to the subject. More detailed information would be needed before making decisions in this complex field. The views and opinions expressed in this paper are those of the consultant and do not necessarily reflect the views of the secretariat of UNIDO.

¹See the Fertilizer Industry Series published by the United Nations Industrial Development Organization (ID/Ser. F, Nos. 1, 2, 3, 4 and 5).



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INTRODUCTION

The selection of projects in developing countries is often dependent on the availability of suitable economical processes. Other significant considerations and reasons for the construction of a basic or intermediate petrochemical plant are:

- (a) To save foreign exchange;
- (b) To provide a nucleus for the growth of other local derivative industries, eventually through which more economic basic and/or intermediate plants can be built;
- (c) To utilize readily available starting materials;
- (d) To add a high value during manufacture in comparison to the required capital investment;
- (e) To be eligible to obtain the necessary government support in the form of tariffs and so on.

This publication is addressed primarily to a government agency or local industrial group evaluating chemical projects and the means and sequences for developing the local petrochemical industry. This frequently differs from the situation of an international oil or chemical company whose considerations include tax concessions, the ease of repatriation of capital, and the merit of attempting to obtain a maximum share of the local market by being the first local producer. The constraints under which the international company operates will often lead to different analyses and conclusions from those arrived at by the government agency of the country. However, both may be "correct solutions" for the country, considering all the circumstances.

Each country and region has unique local factors such as availability of raw materials, population, and degree of development. The variety of such factors prohibits generalizations with respect to the detailed plan to be followed for the development of a basic and intermediate petrochemical industry. In order to obtain a relatively low rate of price inflation and a real growth in the standard of living, a country must try to balance its income, e.g. exports, foreign investment and aid, and expenditures, e.g. goods, services, plant equipment, know-how, repatriated profits (7). In balancing this relationship, it is desirable to invest in the plant and equipment which offers the most value added during manufacture as compared to the amount of investment required. The period of time for repayment of the investment with the money saved on the purchase of raw material and finished goods should be minimized. As a further criterion for a sound project, it is assumed that the tariff level required to insure the competitiveness of the developing country's product should not be greater than 30-40 per cent of the lowest price available in the country of origin. These requirements frequently mean that it will be desirable for a developing country to concentrate initially on the production of end-use chemicals and to import low-value, commodity chemicals.

This is not always the case. For example, countries that have abundant oil and natural gas resources should concentrate on primary petrochemicals because of the significant cost advantage that may be achieved by utilizing inexpensive raw material. This situation tends to prevail in countries of the Middle East, and to a lesser extent, in North Africa, Venezuela and other selected areas.

Exports are always regarded as a possible means for building larger, more economic units in a given country. However, since this has seldom been a successful strategy, exports should not normally be counted on to justify earlier construction of large plants. Even Mexico with its advanced petrochemical industry² has not been able to make significant strides in exporting chemical intermediate and end products.

Recommendations are presented here for selected chemicals of major interest to be considered for manufacture in a developing country. Production economics are presented where two or more processes are competing for possible development.

²Vinyl chloride: 19,500 tons per year in 1967, 74,500 tons per year in 1969 (estimated); low-density polyethylene: 24,000 tons per year in 1966, 75,000 tons per year in 1969 (estimated).

PETROCHEMICALS: METHODS OF PROCESSING AND COST OF PRODUCTION

Acetylene

Developing countries should not generally consider the manufacture of acetylene for strictly chemical purposes since most of the major acetylene derivatives can be produced at a lower cost from ethylene. The traditional acetylene derivatives are vinyl chloride, acrylonitrile, vinyl acetate, acrylic acid, acetaldehyde, trichloroethylene and perchloroethylene, and neoprene. Ethylene has become a more economical feedstock for vinyl chloride, acetaldehyde and acetic acid and may soon be more economical for vinyl acetate. Propylene is now the major feedstock for acrylonitrile. Processes for most of the major derivatives of acetylene (except neoprene) are discussed elsewhere in this paper.

Acrylonitrile should be imported owing to the economies of scale and the substantial royalties required for the Sohio and Distiller processes based on propylene and ammonia. In general, the market for acrylonitrile is small in the developing countries, as is the market for trichloroethylene and perchloroethylene and neoprene. Straight acrylates and acrylic fibres can be made from imported acrylonitrile.

There is often an earlier justification for manufacturing chlorinated solvents than for many other products since chlorine is usually in oversupply. Although acetylene is an excellent feedstock for trichloroethylene and perchloroethylene, it is impossible to justify an acetylene plant solely for this use. Ethylene can now be used as feedstock for trichloroethylene and perchloroethylene; methane or propane are used to make perchloroethylene (and carbon tetrachloride) by a thermal chlorination process.

For those countries that can justify an acetylene plant, the major commercially available processes are calcium carbide, Wulff, BASF (Badische Anilin-und Soda-Fabrik A.G.) partial oxidation, electric arc, Montecatini, SBA (Société Belge de l'Azote)-Kellogg and Kureha. The calcium carbide process is becoming obsolete and the partial oxidation process has been found to be of recent interest only in special cases where low-cost natural gas is available and a large degree of by-product utilization can be attained. The 60,000 tons³ per annum capacity plant recently completed by ICI (Imperial Chemical Industries) using the BASF process is reported to be having considerable trouble (2). The BASF plant is operated primarily for

³Unless otherwise indicated, all tons referred to in this paper are metric tons.

synthesis gas, whereas ICI is attempting primarily to produce acetylene. The electric arc process has only been commercially employed at one installation by DuPont. The Wulff process is probably the most economic large-scale acetylene process offered at this time.

Acetylene and ethylene

The Kureha process consists of partial oxidation of naphtha to yield acetylene and ethylene. These streams are then used for vinyl chloride monomer. This process has found acceptance for a few specific situations where no cracking capacity was available or planned. The economics for vinyl chloride monomer via Kureha are presented under vinyl chloride.

The Wulff process, which can produce both acetylene and ethylene or acetylene alone, has reportedly suffered from start-up difficulties at the British Geon (20,000 tons per year acetylene) and British Oxygen (30,000 tons per year acetylene) plants (5). Plants of Marathon at Burghausen and Konam (Dutch Celanese) at Europoort were starting production at the time this paper was written. Union Carbide is planning a Wulff acetylene-ethylene plant for Brazil with the capacity variously reported between 68,000 and 128,000 tons per year of ethylene and between 16,000 and 35,000 tons per year of acetylene. This plant makes economic sense for Union Carbide since it is the only polyethylene producer and can, at the lower estimate, use all of its ethylene captively. The market in Brazil in 1972 will also be capable of supporting a large-scale ethylene plant based on naphtha and including aromatics recovery. Such a project (200,000 tons per year of ethylene) was being planned by Phillips Petroleum and Petroleo União. Phillips has decided not to proceed, but the project is being taken over by various private firms with the continued support of Petroleo União. Petroguisa, a new Petrobras subsidiary, also has a share in the venture. Without the polyethylene market, however, this project is being delayed.

The economics of a conventional ethylene plant and a Wulff acetylene-ethylene plant (assuming an ethylene-acetylene ratio of 1.07 to 1) are compared in figures 1 and 2 as a function of capacity.⁴ Acetylene and ethylene cannot be compared on a straight pound-for-pound basis since acetylene is a more efficient reactant.

⁴The following assumptions were used in calculating the data presented in figures 1 and 2:

	1967 United States basis
Investment	
Utilities and operating costs	
Electricity	1.7 cents per kilowatt hour
Cooling water	5 cents per thousand gallons
Process water	30 cents per thousand gallons
Fuel	40 cents per million BTU
Steam	\$1.50 thousand per pound
Labour	\$3,000 per annum
Supervision	\$4,500 per annum
	} including benefits
Maintenance, materials and labour	5% of BLCC (Battery limits capital cost)
General plant overhead (including local insurance, taxes etc.)	8% of BLCC
Direct overhead	30% of labour and supervision
Depreciation	10% of BLCC
Return on capital	25% per annum before taxes on total capital, defined as battery limits x 1.45 for off-sites and working capital

(Generally, acetylene can be twice as expensive as ethylene and still remain competitive.) In making the comparison in figure 1, the Wulff ethylene figures should be taken from the conventional ethylene figure. The acetylene value can then be calculated. In this case, with a ratio of 1.07 to 1, ethylene to acetylene, the resulting acetylene price would be 8.3 cents per pound.⁵ In some situations this could be quite attractive, particularly where a new Wulff unit could be located adjacent to an existing vinyl chloride monomer operating on expensive acetylene *ex* calcium carbide.

Ethylene

The processes available for the production of ethylene in a developing country, in addition to standard cracking of naphtha, gas-oil, ethane propane and the mixed acetylene/ethylene processes mentioned above, are the dehydration of ethanol (usually available as a sugar-cane by-product) and for dilute ethylene, the Dianor process recently developed by Chem Systems Inc. (7, 3). The conventional ethylene plant is so highly capital intensive that a plant may have to be sized at 100 to 150 thousand tons per year capacity (still considered small by United States, Western European and Japanese standards) before it can be considered for a developing country. This is based on ethylene available at 3 cents per pound or less from the new 1,000 million pounds per year capacity plants, plus 30 per cent for tariff protection and additional costs for shipping in refrigerated tankers. The shipment of liquid ethylene by ocean-going tankers (1) can only be justified for large quantities or as a temporary solution. The former situation is illustrated by the shipments from ICI from Wilton, England to Rosenburg, the Netherlands, where the costs of docking facilities, refrigerated storage, equipment to maintain the refrigeration value contained in the liquid ethylene at the delivery point, and the size and investment of the ship are spread over a large volume of material. The use of liquid shipment as a temporary solution is illustrated by the temporary shipments from ESSO between Port-Jérôme, France and Stenungsund, Sweden.

What does a developing country do before it attains a market of sufficient size to justify its own ethylene plant? The answer to this can be partially explained by an analysis of the major ethylene derivatives. The largest ethylene users are vinyl chloride and polyethylene. Also of major interest are ethylbenzene for styrene, ethylene oxide for glycols, ethanalamines, glycol ethers, vinyl acetate, etc., and ethylene dichloride for uses such as trichloroethylene, perchloroethylene and ethylenediamine. Some of the above (specifically vinyl chloride and ethyl benzene) can be produced from ethylene which has not been purified to polymer grade requirements.

A typical composition of the ethylene stream from the Dianor process for dilute ethylene mentioned above is shown in table 1.

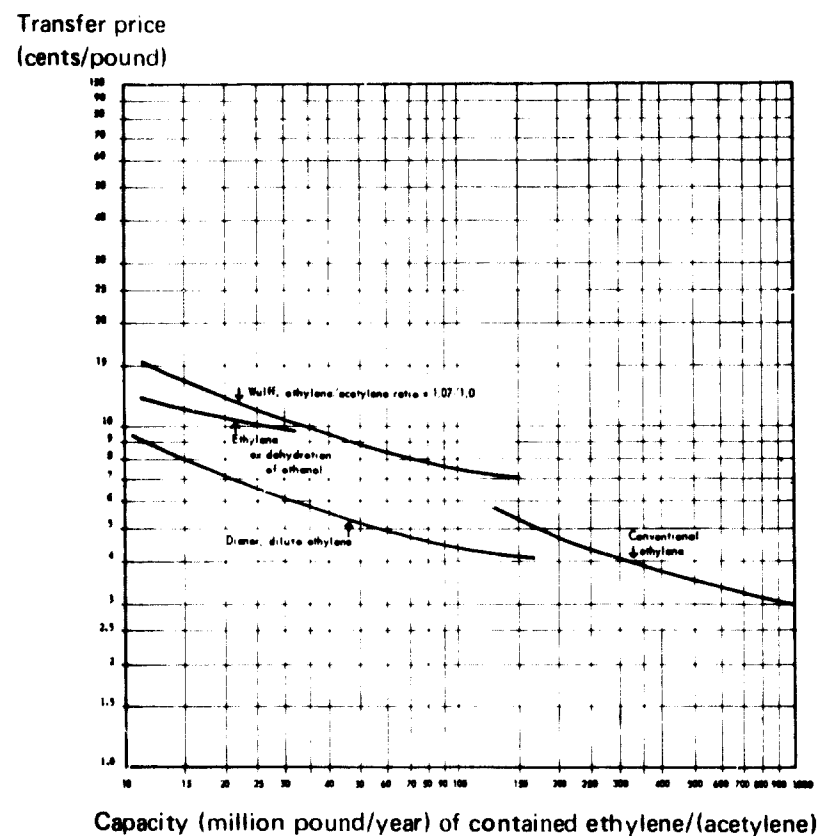
The Dianor process, utilizing a reboiled absorption recovery system rather than distillation (3), claims lower capital and operating costs than those for a high-purity ethylene plant (see figures 1 and 2). As it is possible to produce a grade of ethylene suitable for the production of vinyl chloride and polyvinyl chloride, it is felt that the production of high-purity ethylene and polyethylene can be initially deferred in many cases, particularly in view of the continued depressed world price for

⁵All prices quoted in this paper are in US dollars and cents. One cent (¢) equals US \$0.01.

TABLE 1. TYPICAL DISTRIBUTION OF COMPONENTS IN ETHYLENE STREAM FROM THE DIANOR PROCESS, BY WEIGHT

Component	Per cent of total weight
Hydrogen	1.72
Methane	34.55
Ethylene	57.60
Ethane	6.13
Acetylene	Trace
Propylene	Trace

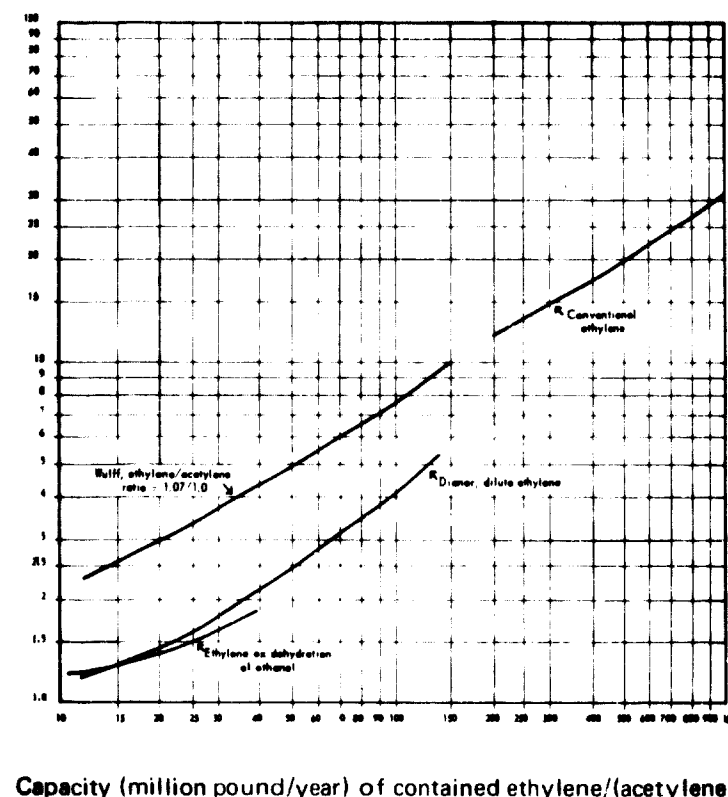
polyethylene and the high capital cost associated with its production. As long as ethanol dehydration is advantageous only as a source of pure ethylene for polyethylene, the establishment of ethanol dehydration plants should also be terminated in developing countries, regardless of the low cost of locally available ethanol. An extremely low price for ethanol (3 cents per pound) has been assumed in the calculations but, as can be seen in figure 1, this route is not competitive even at this low feedstock value.



Notes: Transfer price includes a 25% per annum return on an investment equal to 1.45 times the battery limits investment.
Cost of production based on prices of feedstock, utilities etc. at a South American location.
Straight-run naphtha feedstock.

Figure 1. Ethylene (acetylene) transfer price versus capacity

Battery limits investment
(millions of US dollars)



Notes: Straight-run naphtha feedstock.
U.S. Gulf Coast, 1968 prices.

Figure 2. Battery limits investment versus capacity

Aromatics

The most commonly available aromatics are benzene, toluene and xylenes, which are frequently termed "BTX". The principal chemical uses include:

- Benzene: styrene, phenol, dodecylbenzene, caprolactam, and nylon 6/6
- Toluene: trinitrotoluene, toluene diisocyanate, and benzene
- Xylenes:
 - p-xylene - terephthalic acid for polyesters
 - o-xylene - phthalic anhydride
 - m-xylene - isophthalic acid

Benzene is in greatest demand, particularly since the toluene route to caprolactam has not gained widespread acceptance. The uses for toluene are limited and ultimately its greatest chemical use is as a forerunner for benzene to which it is converted by hydrodealkylation. The demand for both para- and ortho-xylene for the indicated end uses is increasing rapidly to the extent that plants are installed to isomerize m-xylene to para- and ortho-xylene.

Aromatics are principally produced today by the catalytic reforming of selected naphtha cuts. Probably the best known and most widely used process is Universal Oil Products (UOP) platforming, where the relative yields of these three aromatics depend on the quality of the feed to the reformer. Thus, a heavy naphtha will produce more of the heavy aromatics, the xylenes. An alternative source of aromatics is as a co-product in the manufacture of ethylene where it occurs in concentrations of up to 50 per cent in the cracked gasoline when liquid feeds are used.

It is unlikely that the quantities of aromatics available from this source would be sufficient to warrant extraction until the capacity of the ethylene plant is in the region of 100,000 tons per year, at which point corresponding aromatics production would be approximately 30,000 tons per year. A typical distribution of components in cracked gasoline is given in table 2.

Platforming was originally developed in the late 1940s to upgrade low-octane, straight-run gasolines. This was accomplished by reforming the paraffin molecules into aromatics and branched-chain isomers, with a resulting increase in octane number. Platforming is still the most widely used process for upgrading straight-run gasolines, the majority of the aromatics produced remain as motor gasoline and are never extracted as separate products. A typical distribution of components in the effluent from a platformer when processing heavy gasoline is given in table 2.

TABLE 2. TYPICAL DISTRIBUTION OF COMPONENTS IN CRACKED GASOLINE AND HEAVY GASOLINE REFORMATE BY WEIGHT

Component	Cracked gasoline (per cent of total weight)	Heavy gasoline reformate
Benzene	24.2	3.5
Toluene	16.1	19.0
Xylenes	8.1	21.5
Non-aromatics	51.6	40.0
Higher aromatics	—	16.0

The production and recovery of aromatics requires a great investment per unit of production; therefore, the economies of scale to be gained from large capacity plants are important. It is unlikely that a developing economy would be able to obtain such economies of scale to justify aromatics production. However, there is one compromise solution which may prove to be favourable.

As mentioned earlier, platforming is employed for gasoline upgrading. Most refineries producing significant quantities of motor gasoline incorporate a platformer which could be designed for a larger capacity to correspond with the amount of benzene required. Figure 3 shows how the platformer would operate to produce the required quality of motor gasoline, a portion of which would be withdrawn and processed for benzene and toluene extraction. Inspection of table 2 will show that the quantity of toluene produced in a platforming operation is much higher than that of benzene. Therefore, the toluene must be hydrodealkylated in order to produce the required quantity of benzene. Both the extraction and hydrodealkylation steps involve a substantial investment and are unlikely to prove attractive for an ultimate

benzene capacity of less than 20,000 tons per year, even though this flowsheet provides the platformer with some economies of scale. It is most unlikely that the recovery of xylenes, with the subsequent necessity of xylene separation, would prove economic in the capacities required for the economy of a developing country. This material, therefore, which is of high octane number, should be returned to the gasoline pool together with raffinate from the aromatics extraction step.

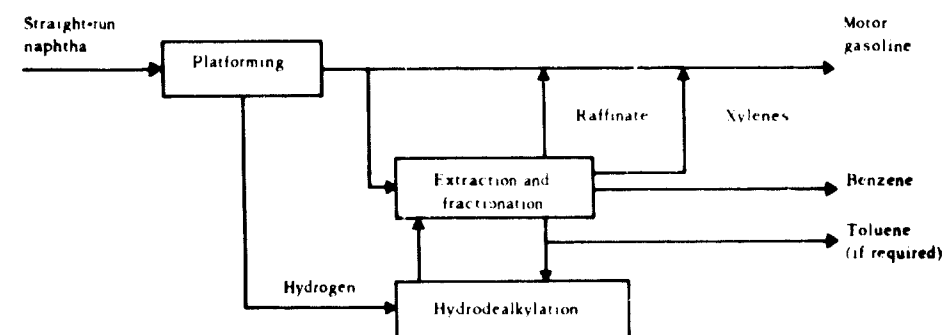


Figure 3. Platforming for gasoline upgrading

The cost of benzene produced by this scheme is 5.6 cents per pound as outlined in table 3. The general assumptions are the same as were made above for figures 1 and 2. The feedstock value is motor gasoline at 2 cents per pound, the feedstock quality is as shown in table 2, and the capacity of benzene is 20,000 tons per year.

TABLE 3. PRODUCTION COSTS FOR BENZENE FROM REFORMATE AND HYDRO-DEALKYLATED TOLUENE^a

	Production costs (cents/lb)
Raw materials	2.0
Utilities	0.9
Labour and supervision	0.05
Maintenance, taxes, overhead	0.5
Depreciation	0.55
Total cost of production	4.0
25% return on total capital	1.6
Transfer price	5.6
	Investment costs (millions of dollars)
BLCC investment:	
De-pentanizer/re-run	0.2
Hydeal	0.5
Extraction (sulpholane)	1.1
Royalties	0.2
Total	2.0

^aThese costs are relevant to a typical plant with a capacity of 20,000 tons per year.

Cyclohexane

Cyclohexane is used almost exclusively in the manufacture of nylon 6/6 and nylon 6. It is converted to adipic acid and hexamethylene diamine (HMDA) for the production of nylon 6/6 and to caprolactam for nylon 6. The manufacture of cyclohexane, therefore, can only be considered when the economy can support a nylon production industry. This will probably only apply in a fairly advanced state of economic development. The bulk of cyclohexane is produced by hydrogenation of benzene, where 0.83 gallons of benzene yields 1.0 gallon of cyclohexane.

The production of cyclohexane is not as capital intensive as aromatics production. The transfer price, nevertheless, is fairly sensitive to the scale of production, as indicated in table 4. The price of cyclohexane is closely linked to that of benzene and the resulting transfer price is very high by international standards. Benzene is priced at 5.6 cents per pound based on table 3. The United States is currently exporting large quantities of low-priced cyclohexane and it will probably be advisable for a developing country to purchase rather than produce until the cost of indigenous benzene becomes competitive with world prices.

TABLE 4. PRODUCTION COSTS FOR CYCLOHEXANE^a

	Costs (cents/lb)	
	14,500 tons/year	29,000 tons/year
Raw material	5.4	5.4
Utilities	0.1	0.1
Labour and supervision	0.1	0.05
Maintenance, taxes, overhead	0.35	0.24
Depreciation	0.35	0.26
Total cost of production	6.30	6.05
25% return on total capital	0.9	0.65
Transfer price	7.2	6.7
BLCC investment (millions of US dollars)	0.76	1.13

^aThese costs are relevant to typical plants with capacities of 14,500 or 29,000 tons per year.

Butadiene, styrene-butadiene rubber (SBR) and polybutadiene rubber

Butadiene is used almost entirely for the production of elastomers and the bulk of this material is used in styrene-butadiene and polybutadiene rubber for the tire industry. The two main sources of butadiene are from the dehydrogenation of refinery butylene and butanes and as a co-product in the production of ethylene

from liquid feedstocks. A dehydrogenation route has been employed mainly in the United States where ethylene has been derived almost entirely from gas feedstocks (ethane and propane). In Europe, however, almost all ethylene is derived from liquid feedstocks; hence, almost all European butadiene is extracted from the co-product mixed C₄ streams.

Butanes, and particularly butylenes, are generally available in refineries from catalytic cracking and reforming operations. At first sight it might appear advantageous to dehydrogenate these materials for butadiene. The dehydrogenation route, however, is an expensive operation involving a very large capital investment and cannot be justified in small capacities. As an approximate yardstick, it is considered unlikely that a dehydrogenation plant with a butadiene capacity of less than 40,000 tons *per annum* would prove to be economical. The investment cost at this level would be in the region of \$15 million. Where ethylene is being produced from liquid feedstocks, therefore, it will always be more advantageous to extract butadiene from the mixed C₄ stream rather than employ dehydrogenation.

At the high-cracking severities generally employed today, the gross production of ethylene amounts to approximately 33 weight per cent from a typical full-range naphtha. The corresponding butadiene production is approximately 3.6 weight per cent giving an ethylene to butadiene ratio of about 9 to 1. Butadiene can be recovered from the mixed C₄ product stream by a relatively simple extractive distillation step using one of the well-established solvents such as acetonitrile or furfural. Local circumstances will determine the minimum economic capacity, but it is unlikely to be less than 5,000 tons per annum of butadiene even in a remote location. Thus, the production of butadiene cannot be justified unless there is a demand for ethylene of 50,000 tons per annum or more. The alternative use for the mixed C₄ stream is a fuel and it is reasonable, therefore, in an economic assessment, to charge the mixed C₄ feedstock at fuel value. The approximate battery limits investment cost for such an extraction plant is \$950,000 and the corresponding butadiene transfer price is calculated at 8.2 cents per pound as outlined in table 5. At this level and under these circumstances, butadiene extraction begins to look attractive.

A developing country, therefore, must either have a major automobile market in order to justify a dehydrogenation unit (approximately 40,000 tons of butadiene per year) or be sufficiently advanced to require approximately 50,000 tons of ethylene per year in order to extract butadiene as a by-product, before it can consider butadiene production. Brazil is an interesting but exceptional case in point. Brazil has a large automobile population for a developing country. This market, centred principally in the states of São Paulo and Guanabara, has recently justified an SBR plant (1962) and a butadiene-by-dehydrogenation plant (1967). SBR was imported until the market reached approximately 20,000 tons per year. Then, through internal market requirements and exports (up to 16 per cent of total production in 1963-1965), the plant was able to operate at 75 per cent of its 40,000 tons per year capacity within two years after start-up. The capacity of the dehydrogenation type of butadiene plant is 33,000 tons per year. Sales contracts have apparently been established with other LAFTA (Latin American Free Trade Association) countries to use some of Brazil's butadiene supply until the internal demand in Brazil is sufficient to keep the plant operating close to capacity. This is an interesting case, but few other developing countries will have the automobile population to justify the dehydrogenation route prior to having an ethylene requirement of 50,000 tons per year.

Butadiene from fermentation ethanol by two-step dehydrogenation via acetaldehyde is no longer economical in comparison to the process described above. To cite Brazil again, it is of interest that Brazil obtained such a plant in used condition as well as a plant for 30,000 tons per year of *cis* 1,4 polybutadiene and installed them by 1965. A lack of market, among other factors, has prevented the plant from ever reaching more than 25 per cent of capacity. The fact that ethanol is available at very low (subsidized) prices is now irrelevant.

TABLE 5. PRODUCTION COSTS FOR BUTADIENE VIA EXTRACTIVE DISTILLATION OF MIXED C₄

	<i>Costs (cents/lb)</i>
Raw materials	0.9
Utilities	1.3
Labour and supervision	0.3
Maintenance, taxes, overheads	1.2
Depreciation	1.3
Total cost of production	5.0
25% return on total capital	3.2
Transfer price	8.2
BLCC investment (millions of US dollars)	0.95

^aThese costs are relevant to a typical plant with a capacity of 5,000 tons per year.

Cumene

Cumene (isopropyl benzene) is not a favoured product for manufacture in developing countries for the following reasons:

- (a) Its low value; major producers in developed countries think of cumene as a way to remove benzene;
- (b) The large amounts of by-product acetone produced for which there is generally a much smaller market than for phenol which is the major outlet for cumene;
- (c) If phenol is going to be produced in a developing country, the modified Raschig process (based on chlorine) is more economical in most cases.

The production of cumene is occasionally considered by developing countries since there is sometimes a considerable excess of dilute propylene (60 per cent propylene, 40 per cent propane) available from refineries and this can be used for the synthesis of cumene. This stream is also of adequate purity for the production of acetone via isopropanol, as pointed out below, but these considerations are minor compared to the economies of scale.

Propylene

Propylene is in the same category as ethylene in terms of investment timing for a major plant in a developing country. The refinery by-product stream can satisfy those propylene by-product markets which can justify a plant such as propylene oxide (by chlorohydrin, possibly in connexion with ethylene oxide as discussed below) and propylene tetramer. The other end uses, e.g. polypropylene, cumene, acrylonitrile, 2-ethylhexanol, and heptene, are preferably imported if required until the economy has grown beyond the status of that of a developing country. Tetramer is cited as a market for propylene despite the fact that its major market is dodecylbenzene, which is used mostly in non-biodegradable detergents, since the C₁₄ stream required for the competitive biodegradable detergents is not generally available.

Propylene is produced as a by-product in refinery catalytic cracking processes and as a by-product in ethylene manufacturing. Where the demand for motor gasoline is critical and many refinery operations are designed to produce gasoline from heavier material, the production of refinery propylene is high. This is the case in the United States. In Europe, however, the refineries are not so heavily geared to gasoline production. However, since ethylene production is predominantly based on liquid feedstocks, the bulk of propylene is derived from the latter source (8).

Refinery propylene is generally produced at about 60 per cent purity. This can be employed as it stands for certain chemical manufacture, e.g. propylene oxide and tetramer, but generally it is more economical to convert it into high-octane motor gasoline by alkylation or catalytic polymerization. If propylene is derived from ethylene production as a by-product, it will be approximately 93 per cent pure and can then be used for chemical manufacture or can be upgraded to 99 per cent purity (polymer grade) without great additional expense.

The demands of a typical developing country will not be adequate to justify these purity levels; however, the refinery grade material is adequate for the few propylene derivatives important for developing countries.

Polyvinyl chloride, ethylene dichloride and polyethylene

Polyvinyl chloride (PVC) is recommended as the first plastic for developing countries in preference to polyethylene or polystyrene. The properties and use patterns are presented in several articles (10, 11). One of the recent papers, "Effects of Production Scale and Changing Technology" (11), presented at the November 1967 meeting of the Association of Industrial Chemical Engineers (A.I.Ch.E.) is a good summary of the economics of large-scale plants. Except for the superiority of polyethylene in electrical insulation and certain injection moulded products, PVC is equal to and, in many cases, superior to polyethylene in properties. PVC is particularly good for many of the products which are important for developing countries, such as flooring, pipe and conduit, film and sheet, rigid bottles, coatings, clothing, footwear and house furnishings. The investment required for PVC is much less than that for polyethylene as will be discussed below.

Table 6 below presents an estimate of the economics for vinyl chloride monomer (VMC) using ethylene and acetylene as feedstocks.

TABLE 6. PRODUCTION COSTS FOR VINYL CHLORIDE MONOMER^a

	Costs (cents/lb)				
	<i>Dianor dilute ethylene</i>	<i>Wulff acetylene</i>	<i>Carbide acetylene</i>	<i>Ethylene from ethanol</i>	<i>Kureba mixed feed</i>
<i>Ethylene/acetylene production</i>					
Net feedstock cost	1.68	3.31	21.40	5.50	See below
Utilities	0.92	0.53	0.02	0.80	
Labour and supervision	0.28	0.14	0.14	0.14	
Maintenance, depreciation, taxes, overheads	2.16	5.14	1.78	2.00	
Total hydrocarbon cost	5.04	9.12	23.34	8.44	
<i>Vinyl chloride monomer production</i>					
Net feedstock cost	4.20	4.91	11.01	5.80	3.10
By-product credit	(0.14)				
Utilities	1.01	0.20	0.20	0.86	1.90
Labour and supervision	0.01	0.05	0.05	0.05	0.40
Maintenance, depreciation, taxes, overheads	1.13	0.99	0.99	1.24	2.50
Total manufacturing cost of vinyl chloride	6.21	6.15	12.25	7.95	7.90
25% return on BLCC investment	2.34	3.74	2.02	2.60	2.80
Vinyl chloride transfer price	8.55	9.89	14.27	10.55	9.90
BLCC investment (millions of US dollars)	3.32	5.3	2.8	3.7	4.0

^aThese costs are relevant to a typical plant with a capacity of 12,700 tons per year.

It was stated above that polyethylene requires a considerably greater investment than PVC. This is evident from the figures in table 9, where the investment costs for 24,000 tons per year of polyethylene and PVC are compared. Polyethylene is derived from ethylene *via* ethanol in case 1 and from its necessary share of a 200 million pounds per year conventional ethylene plant in case 2. PVC is derived from VCM *via* Dianor process using naphtha feed in case 3 and from VCM *via* a Wulff mixed ethylene/acetylene plant with naphtha feed in case 4. The lowest investment required in manufacturing a basic plastic in a developing country is *via* the Dianor vinyl chloride process. The lowest investment polyethylene from a comparable feedstock is approximately 60 per cent higher and the Wulff mixed ethylene/acetylene route to VCM requires 30 per cent more capital investment.

As developing countries convert to the production of VCM by direct chlorination of ethylene (whether dilute or concentrated) to ethylene dichloride (EDC), followed by EDC cracking, ethylene dichloride, of course, becomes available as a valuable reactive intermediate.

Small markets are always a problem, and this is particularly true when considering the construction of polymer plants in developing countries. The statistics for Colombia, for example, are given in table 7. In Israel, which is at a more advanced state of development, a small market limits production facilities for plastics and related materials as indicated in table 8.

TABLE 7. PLASTICS INDUSTRY IN COLOMBIA

	Production (tons/year)		Capacity (tons/year)	
	1963	1964	Available (1966)	Under constr.
<i>Plastic material</i>				
Polyethylene	—	—	—	15,000
Polyvinyl chloride	—	—	12,000	6,000
Polystyrene	—	—	3,000	
Polyvinyl acetate	2,200	2,700	not available	not available

TABLE 8. PLASTICS INDUSTRY IN ISRAEL, 1966

Product	Capacity (tons/year)	Raw material base
Ethylene	15,000	Refinery gas, naphtha
Ethylene dichloride	—	Ethylene, chlorine
Polyethylene	6,500	Ethylene (above)
Polyvinyl chloride	7,000	Ethylene dichloride
Polyvinyl acetate emulsions	Capacity not available	From imported monomer

Source: Derived from data in *Chemische Industrie*, December 1966.

The two examples above illustrate the great difficulty that would be encountered in constructing a conventional ethylene plant in these countries in order to supply the small polymer plants. However, in both Colombia and Israel, local national oil companies decided to build small ethylene plants to start a local petrochemical industry.

TABLE 9. BATTERY LIMITS CAPITAL COSTS FOR POLYETHYLENE AND POLYVINYL CHLORIDE INCLUDING BACK-UP BATTERY LIMITS CAPITAL FOR ETHYLENE, ACETYLENE, VINYL CHLORIDE MONOMER^a

	Costs (millions of US dollars)			
	Polyethylene		Polyvinyl chloride	
	Case 1 ^b	Case 2 ^b	Case 3 ^b	Case 4 ^b
Hydrocarbon plant	2.2	2.7	1.6	3.3
Vinyl chloride monomer plant	—	—	2.1	2.3
Polyvinyl chloride plant	—	—	3.0	3.0
Polyethylene plant	8.4	8.4	—	—
Total	10.6	11.1	6.7	8.6

^aThese costs are relevant to a typical plant with a capacity of 24,000 tons per year.

^bCase 1 — polyethylene from ethylene via ethanol
Case 2 — polyethylene from conventional ethylene
Case 3 — PVC from VCM via Dianor process using naphta feed
Case 4 — PVC from VCM via Wulff mixed ethylene/acetylene plant with naphta feed.

Ethylbenzene, styrene, polystyrene

Polystyrene is a particularly versatile plastic and should initially be imported to developing countries. This permits the local moulding, extruding and fabricating industry to learn to use the polymer and develop the markets. As soon as can be economically justified, at a capacity of approximately 7,500 to 10,000 tons per year, a general-purpose polystyrene plant can be installed. After a second polystyrene plant has been built, a styrene and an ethylbenzene plant, based on the alkylation of benzene, can be built. The ethylbenzene-styrene plant should have a capacity of at least 20,000 to 25,000 tons per year. The benzene will still be imported at this stage, but the ethylene will be produced locally from one of the sources mentioned above. High-purity ethylene is not required. The minimum economic sizes recommended above are based on the requirement of being competitive with 30 per cent tariff protection.

It is interesting to trace the trends which have been established in the selection of size of a styrene monomer plant. In the first place, outside with the exception of a very small Dow plant commissioned in the 1930s and possibly some of the earlier

I.G. Farben plants, the initial major investment in styrene plants was in relatively large units (approximately 25,000 to 50,000 long tons per year capacity), which is most unusual for a newly developed chemical industry.

The styrene plants in the United States were installed in a great hurry during the Second World War with a complete interchange of technical information among process developers and manufacturers. Owing to haste, these plants were not necessarily well optimized. As a consequence, it has been the general procedure in the United States to expand the original plants by eliminating obstructions. Such expansion has taken place in the post-war era with a minimum capital investment.

On a world-wide basis, a substantial number of post-war styrene plants have been installed which were smaller than some of the original plants (particularly the expanded ones). The smaller plants were in part justified by the limited rate of market growth or by the limited raw materials. This was the case in areas in Europe and Asia where such plants were installed. A number of smaller-scale plants have also been justified in the United States in the post-war era, some of them by the existence of captive sources of low-cost benzene and ethylene or captive consumption of the product, others because of the use of an inexpensive ethylbenzene feedstock distilled from low-cost xylene mixtures.

While the continued expansion of styrene plants on a scale close to the size of the plants constructed during the Second World War (i.e. approximately 50,000 long tons per year) is still under way around the world, there is definitely a trend towards larger-sized plants. Various 200 to 500 million pounds per year capacity plants have already been announced for developed countries.

Table 10 lists the production costs for 2,500 and 10,000 tons per year capacity polystyrene and 25,000 tons per year capacity styrene monomer plants. The general cost assumptions for table 10 are the same as those listed for figures 1 and 2. Since the polystyrene plant should be built earlier than the styrene unit, the plant would initially have a raw material cost of about 10 to 12 cents (including freight), assuming that the developing country would impose no tariff, would seek the lowest world price (possibly a dumping price), and would only need to add shipping costs. It can be seen that the 2,500 tons per year capacity plant has almost the same transfer price as the plant four times its capacity. The smaller plant is the base unit for the multipurpose thermoplastic resin plant described below.

The benzene cost in table 10 is 3.8 cents per pound (3.3 cents plus 15 per cent for shipping etc.) and the ethylene price is 4.5 cents per pound (probably possible via local production by the time a styrene monomer unit is built). For this 25,000 ton per year capacity plant, the total operating costs are approximately 2.7 cents per pound for a South American location.

TABLE 10. PRODUCTION COSTS FOR GENERAL-PURPOSE POLYSTYRENE^a AND FOR STYRENE FROM BENZENE^b (VIA ALKYLATION TO ETHYLBENZENE)

	Costs (cents/lb)		
	Polystyrene (2,500 tons/year)	Polystyrene (10,000 tons/year)	Styrene (25,000 tons/year)
Net raw materials	10.5	10.5	4.9 ^c
Utilities	0.4	0.4	1.6

Table 10 (continued)

	Costs (cents/lb)		
	Polystyrene (2,500 tons/year)	Polystyrene (10,000 tons/year)	Styrene (25,000 tons/year)
Labour and supervision	0.8	0.2	0.1
Maintenance, taxes, overheads	2.1	1.3	1.0
Depreciation	1.4	0.8	0.7
Total cost of production	15.2	13.2	8.3
25% return on total capital	4.9	3.2	2.7
Transfer price	20.1	16.4	11.0
BLCC investment (millions of dollars)	0.75	2.0	4.0

^aThese costs are relevant to typical plants with capacities of 2,500 and 10,000 tons per year.

^bThese costs are relevant to a typical plant with a capacity of 25,000 tons per year.

^cBased on ethylene at 4.5 cents per pound and benzene at 3.8 cents per pound.

The battery limits investment for a general-purpose polystyrene plant with a capacity of 25,000 tons per year, including the ethylbenzene-styrene plant and the necessary share of a Dianor dilute ethylene plant of 80 million pounds per year capacity, is 8.4 million dollars (see table 11). This compares favourably with a plant for the same quantity of polyethylene, but requires higher capital than for an equivalent amount of polyvinyl chloride (see table 9).

TABLE 11. BATTERY LIMITS INVESTMENT REQUIRED FOR POLYSTYRENE INCLUDING STYRENE AND ETHYLENE PLANT BACK-UP INVESTMENTS^a

	Costs (millions of US dollars)
Share of ethylene plant	0.7
Styrene plant	4.1
Polystyrene plant	3.6
Total	8.4

^aThe costs are relevant to a typical plant with a capacity of 25,000 tons per year.

Of the processes available for ethylbenzene, the alkylation of benzene by ethylene was chosen since the direct recovery of ethylbenzene from the C₈ aromatics fraction of naphtha reformat involves an expensive high grade of purification which is economically feasible only in conjunction with extensive reforming capacity and suitable equipment for the recovery of individual xylenes. The benzene alkylation

process is available from Badger (technology from Badger-Cosden-Union Carbide), Shell/Scientific Design, and Universal Oil Products. The alkylation is typically a Friedel-Crafts type reaction with an AlCl₃ catalyst, although the UOP alkylation uses a BF₃ promoter. High conversion ethylbenzene dehydrogenation processes are available from the four manufacturers listed above. The newer processes have raised the traditional 40 per cent conversion level to the range of 60 per cent.

Chlorinated solvents

Historically the developing countries have manufactured carbon tetrachloride from carbon disulfide as their entry into chlorinated hydrocarbons. This has been largely a result of the availability of carbon disulfide as a by-product from the production of rayon.

Since the demand for caustic soda in the developing countries is usually high in comparison to chlorine, the local manufacture of chlorinated derivatives is often profitable at relatively small production capacities.

The most important chlorinated solvents are carbon tetrachloride, trichloroethylene and perchloroethylene. Carbon tetrachloride has been largely displaced as a general solvent by the other two materials owing to the dangers inherent in handling such a highly toxic material. Much of the carbon tetrachloride produced in the technologically mature countries is used as a chemical intermediate in the production of fluorinated derivatives.

The production of trichloroethylene and perchloroethylene should be an interesting venture in some developing countries. The technology of production of these materials from acetylene is quite simple and available to industry. The physical plants are primarily of carbon steel construction and can often be built locally without large foreign exchange expenditures.

The primary uses for these two solvents are industrial cleaning and dry-cleaning. Industrial cleaning is the area of major interest in the developing countries. Vapour degreasing is the most efficient method for removing oils from fabricated metal parts and is utilized in virtually every metal fabricator and electronic manufacturing operation.

The need for acetylene, either calcium carbide or hydrocarbon based, for metal-cutting operations, together with the availability of inexpensive chlorine, indicates that the manufacture of trichloroethylene and/or perchloroethylene should be seriously considered in many areas with developing metal or electronic fabrication industries.

Table 12 lists the approximate market projections for Australia and Brazil where there are considerably larger markets than in the typical developing country.

Australia has a 10,000 ton per year capacity carbon tetrachloride and perchloroethylene plant based on thermal chlorination of methane and propane. This plant is owned by Imperial Chemical Industries of Australia and New Zealand (ICI/ANZ). The trichloroethylene needs in Australia are supplied by imports. There is a carbon tetrachloride plant of 2,200 tons per year capacity based on carbon disulfide in Brazil, operated by IRF Matarazzo, S. A., and a trichloroethylene plant with a capacity of 5,000 tons per year owned by Electrocloro Industrias Químicas, S. A.

TABLE 12. ESTIMATED CONSUMPTION OF CHLORINATED SOLVENTS IN BRAZIL AND AUSTRALIA, 1965, 1967 and 1970

	Brazil (tons/year)		Australia (tons/year)	
	1965	1970 <i>est.</i>	1967	1970 <i>est.</i>
Carbon tetra- chloride	2,200	3,200	6,000	9,000
Trichloroethylene	2,700	5,500	5,000	7,500
Perchloroethylene			2,500	3,000

The current trend in the United States, Europe and Japan is to manufacture trichloroethylene from ethylene or ethylene dichloride rather than from acetylene. However, even in the United States, the great bulk of trichloroethylene is still acetylene based.

Ethylene and propylene oxide and glycols

Ethylene and propylene oxides are important intermediates with a large number of derivatives and end uses. These products are generally produced at an intermediate stage in the development of a chemical industry in a country, with ethylene oxide being of greatest interest.

The most important ethylene oxide derivatives are glycols and non-ionic surfactants, with glycol ethers and ethanolamines also being significant. Propylene oxide is mostly used in propylene glycols and in polyols for polyurethanes. Ethylene oxide is produced by the oxidation of ethylene by air, as well as oxygen over a silver catalyst. Similar processes have been announced for propylene oxide, which is also still produced by the traditional chlorhydrin process which was also the original route to ethylene oxide.

An interesting set-up for a developing country would involve a combined unit for the production of ethylene and propylene oxide via the chlorhydrin process. The plant and some of the derivative units can be run on a campaign basis, with the possibility of producing, for example, ethylene oxide and derivatives for three months, and then propylene oxide and derivatives for two months. This approach has the advantage of minimizing the capital cost disadvantage of small units by combining the two plants and is particularly attractive if chlorine prices are low.

As the market grows, an oxidation plant, preferably using air, for ethylene oxide could be constructed and the chlorhydrin plant dedicated solely to the production of propylene oxide. A combined chlorhydrin plant, for example, with a capacity of 20 to 25 million pounds per year of total oxide, could be viable in many situations. A conventional ethylene oxide plant is generally not viable at anything less than 20 to 25 million pounds per year although this is dependent on the cost of ethylene raw material and the import costs and duties for ethylene oxide derivatives.

The cost of production for ethylene and propylene oxide with an equal time share of the single chlorhydrin reactor is given in table 13. The average transfer

price, based on the same general assumption as for figures 1 and 2, for a 24 million pound per year campaign operation is 13 cents per pound, a price which compares favourably with current world prices of 10 cents per pound and 12 cents per pound for ethylene oxide and propylene oxide respectively. The feed prices assumed were 3 cents per pound for propylene (only low-purity 60/40 refinery grade propylene is required), 4.5 cents per pound for ethylene (high purity is not required) and \$30 per ton for chlorine. The low cost of chlorine in developing countries is the real key to the continued strong competition of the chlorhydrin ethylene oxide process with the newer direct oxidation process.

TABLE 13. PRODUCTION COSTS FOR CAMPAIGN ETHYLENE OXIDE, PROPYLENE OXIDE VIA CHLOROHYDRIN^a

	Costs (cents/lb)
Raw materials	7.5
Utilities	1.5
Labour and supervision	0.3
Maintenance, taxes, overheads	0.8
Depreciation	0.6
Total cost of production	10.7
25% return on total capital	2.3
Transfer price	13.0
BLCC investment (millions of US dollars)	1.55

^aThese costs are relevant to a typical plant with a capacity of 24 million pounds per year.

The economics for an 11 million pounds per year capacity ethylene glycol plant with a ratio of approximately 90/8/2 (mono/di/tri) is presented in table 14. The average transfer price compares favourably with world prices of 9.0, 11.0, and 11.5 cents per pound respectively. Polyols, produced by reacting propylene oxide with glycerol, can be produced economically in as small a capacity operation as 10 million pounds per year and are key ingredients for polyurethanes, which offer a potentially low-cost building insulation material.

TABLE 14. PRODUCTION COSTS FOR ETHYLENE GLYCOLS^a

	Costs (cents/lb)
Raw materials	9.9
Utilities	0.9

Table 14 (continued)

	Costs (cents/lb)
Labour and supervision	0.3
Maintenance, taxes, overheads	0.9
Depreciation	0.7
Total cost of production	12.7
25 % return on total capital	2.4
Transfer price	15.1
BLCC investment (millions of US dollars)	0.76

^aThese costs are relevant to a typical plant with a capacity of 11 million pounds per year.

Acetone

Although it would not be feasible economically for a developing country to produce cumene or to import cumene for phenol as discussed above, it is also difficult for a developing country to justify the production of acetone on a small scale from propylene *via* isopropanol. Acetone prices are quite low in the developed countries, e.g. currently 5.5 cents per pound in Europe. They should continue to remain low despite occasional rumours of propylene shortages. The chemical and polymer uses are small in comparison to the amount of propylene used for upgrading motor gasoline as discussed above.

Using even a relatively low propylene price in table 15 (2.5 cents per pound), acetone for a 50 million pound per year capacity plant has a transfer price of 10.4 cents per pound, almost 100 per cent more than the price available in a developed country. These costs are relevant to a plant whose size far exceeds the requirements of a developing country. The basis for computing costs is the same as in figures 1 and 2. Thus, developing countries should import acetone.

Acrylic esters and acrylonitriles

Almost all acrylates produced are subsequently polymerized, either alone or with one or more of many other monomers. The major uses for such copolymers are in paints, coatings for textiles, leathers and paper, various thickeners, floor polishes, elastomers and rug backings.

Methyl methacrylate polymer is cast and extruded into sheets with excellent optical properties, e.g. Plexiglass^R, Lucite^R, and Perspex^R. Such materials replace glass in glazing, are used for various transparent protective installations, such as lenses in automotive lighting, and are important for display signs.

TABLE 15. PRODUCTION COSTS FOR ACETONE FROM PROPYLENE VIA ISO-PROPANOL^a

	Costs (cents/lb)
Raw materials	2.3
Utilities	2.5
Labour and supervision	0.2
Maintenance, taxes, overheads	1.2
Depreciation	1.0
Total cost of production	7.2
25 % return on total capital	3.4
Transfer price	10.6
BLCC investment (millions of US dollars)	4.75

^aThese costs are relevant to a typical plant with a capacity of 50 million pounds per year.

The major synthetic acrylic fibres such as Orlon^R are copolymers of acrylonitrile and other monomers, where acrylonitrile makes up a large portion of the material. The Sohio technology for the production of acrylonitrile from ammonia and propylene has resulted in a substantial reduction in acrylonitrile costs. The best initial strategy for the developing countries seems to be the manufacture of acrylic fibres from a purchased monomer. Such a fibre plant could probably be justified at a capacity of approximately 8 million pounds per year. Manufacturing and investment cost indices for several acrylic fibres have been indicated (14). A monomer plant might be considered feasible at about 50 million pounds per year.

Acrylic acid and its lower esters are produced by several methods. The largest production facility is owned by Union Carbide which uses technology developed by Distillers in England. The process is based on direct oxidation of propylene. Union Carbide has exclusive rights to this process in the United States and Canada. A similar process is offered for licence by Japan Catalytic. Rohm and Haas produce these materials from acetylene using Reppe chemistry, other producers use the ethylene cyanohydrin process and the Goodrich process based on β -propiolactone.

Much of the know-how in acrylate technology is very closely guarded. The end use pattern, with the exception of fibres, is of considerable size only in the highly developed countries. This area would prove difficult to enter for any new producer and seems to be of only marginal interest in the developing countries.

Phthalic anhydride

Phthalic anhydride is a very fast growing intermediate whose major volume derivatives are alkyd resins primarily used for coatings, unsaturated polyester resins

whose major use is in fibreglass reinforced plastics, and plasticizers primarily used for polyvinyl chloride. The former feedstock was high-purity coal-tar-based naphthalene, but recent trends in the past several years have been to o-xylene because of a relative shortage of naphthalene.

Three types of reactors have been developed for phthalic: fixed-bed, fluid-bed and liquid-phase. The fixed-bed reactors are limited by mechanical fabrication capability, and reactors with a diameter of fifteen feet and a capacity of a nominal 6,800 tons per year have been the maximum size. Recent high space velocity catalyst developments by BASF and others have resulted in claims of large potential gains in through-put for the many fixed-bed reactors now in operation. These fixed-bed reactor systems have been licensed and built by Chemiebau and Lurgi using von Heyden technology and by Koppers using Ruhrol technology. Scientific Design has a similar process based on its own developments.

Because of the capacity limitations of the fixed-bed reactors, fluid-bed reactors have been developed by American Cyanamid, Sherwin-Williams (with Badger) and Monsanto. Since the fluid-bed catalyst system is more sensitive, it has been necessary until recently to use high-purity coal-tar naphthalene or petronaphthalene. Badger (Sherwin-Williams process) and Monsanto have apparently solved the problem. Recent announcements indicate that the fluid-bed process will be used for plants with capacities as low as 20 million pounds per year. The liquid-phase process should also offer better economics than the fixed-bed system for higher capacities. Amoco and Progil are both reported to have liquid-phase processes almost ready for commercialization.

Table 16 presents the manufacturing costs for 2,500 and 5,000 tons per year capacity phthalic plants operating on o-xylene feed at a delivered price of 6 cents per pound. A low space velocity catalyst is assumed. The other cost assumptions are as indicated in figures 1 and 2. The transfer prices are 17.7 cents and 14.2 cents per pound which compare with the world price which has decreased from 20 cents per pound in 1958 to below 9 cents per pound in 1963 and which is currently in the range of 11 to 13 cents per pound. Plants in the capacity range of 5,000 tons per year can be justified in developing countries. A considerable number of smaller plants have been built and are operating now. The volatility of the price of phthalic anhydride, which has been purely a result of supply and demand balance, has made small plants look sometimes competitive, sometimes not, depending on the world availability at any given moment.

TABLE 16. PRODUCTION COSTS FOR PHTHALIC ANHYDRIDE^a

	Costs (cents/lb)	
	2,500 tons	5,000 tons
Raw materials	6.6	6.6
Utilities	1.0	1.0
Labour and supervision	1.0	0.5
Maintenance, taxes, overheads	2.3	1.5

Table 16 (continued)

	Costs (cents/lb)	
	2,500 tons	5,000 tons
Depreciation	1.5	1.0
Total cost of production	12.4	10.6
25% return on total capital	6.6	4.9
Transfer price	19.0	15.5
BLCC investment (millions of US dollars)	1.0	1.5

^aThese costs are relevant to typical plants with capacities of 2,500 and 5,000 tons per year.

Ammonia

A great deal of material has been published about ammonia and much thought has been given to the minimum economic capacity of production which can be justified in a developing country. No clear picture emerges since economic criteria that apply to other chemicals cannot be applied to a necessity such as ammonia. Shipping costs to remote agricultural centres can often justify extremely small plants. Probably the most authoritative opinions were expressed at the conference on the Development of the Fertilizer Industry in Asia and the Far East sponsored by the United Nations and held in Bombay in November 1963. The general opinion at this conference was that the most economic capacity for developing countries would be single-train plants with a capacity of 125 to 150 tons of ammonia per day. It should be noted, however, that small capacity plants of around 75 tons per day are still being built to satisfy special local demands.

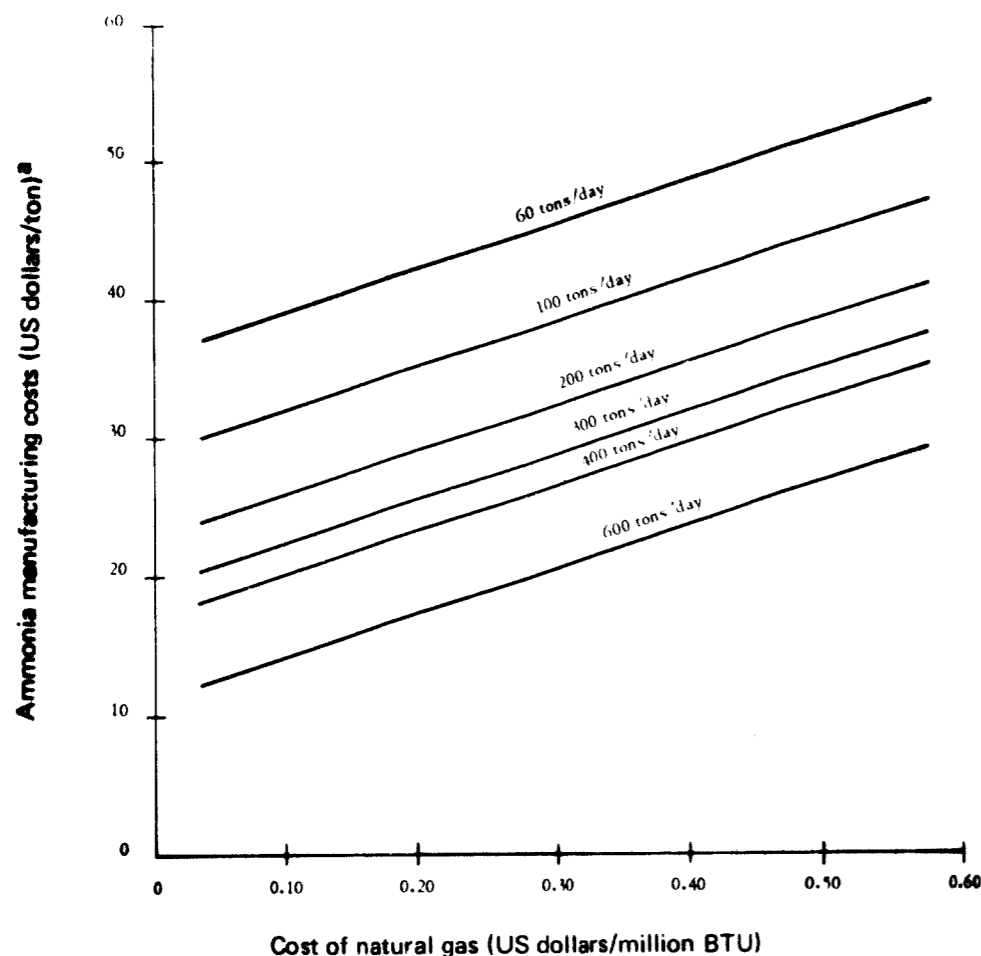
The production cost of ammonia is very dependent upon the type and cost of feedstock and the capacity of production. Figures as low as \$24 per ton (12) ammonia have been achieved from natural gas feedstocks in plants of 1,000 tons per day capacity, while figures of approximately \$40 per ton can be expected from naphtha feedstock at a capacity of about 350 tons per day. The relationship of ammonia production cost with feedstock price and capacity is clearly demonstrated by figure 4 which indicates that at low capacities the production cost could be above \$50 per ton.

Methanol

Immediately after deciding to install ammonia production, it is possible to look at the production of several other important basic chemicals. First is methanol which

employs the same synthesis gas as is produced for ammonia. The main outlet for methanol is formaldehyde, which in turn is made into a variety of resins.

Second is urea which can employ the carbon dioxide rejected from ammonia synthesis to react with ammonia. However, the investment cost for the manufacture of urea is high and the process cannot generally be justified in a developing country until the capacity is substantial. Introduction of these chemicals will require an increase in the facilities for the production of synthesis gas which at the same time will benefit from considerations of increased capacity.



^aThe tons referred to in this figure are short tons, 2,000 pounds per ton.

Figure 4. Manufacturing cost of ammonia made from natural gas at various single-train capacities

About the smallest methanol plant that should be considered is in the capacity range of 30,000 tons per annum. Unfortunately it is not possible with this capacity to take advantage of some of the latest technological developments such as centrifugal compressors with an integrated heat recovery system. The combined effect of scale plus technological consideration makes methanol from small capacity plants almost twice as costly as that produced in the very large plants recently announced in the United States. If one employs the higher feedstock and utility costs

that generally prevail in developing countries, this figure could be even higher. The production costs to be expected in a developing country are given in table 17.

TABLE 17. PRODUCTION COSTS FOR METHANOL FROM NATURAL GAS FEEDSTOCK^a

	Costs (cents/lb)
Natural gas (including fuel)	0.70
Utilities (including catalysts)	0.85
Labour and supervision	0.08
Maintenance, taxes, overheads	0.73
Depreciation	0.57
Total cost of production	2.93
25% return on total capital	1.41
Transfer price	4.34
BLCC investment (millions of US dollars)	2.30

Source: Derived from data in *European Chemical News*, September 30, 1966.

^aThese costs are relevant to a typical plant with a capacity of 30,000 tons per year.

Formaldehyde

Since a large proportion of methanol will be converted to formaldehyde, these two chemicals should be observed together. There are a number of processes available for the production of formaldehyde including those licensed by Montecatini, Reichold, ICI and Procter. All of these involve the oxidation of methanol with air in the presence of steam. The differences lie in the type of catalyst, some of which are iron molybdenum and some silver.

Formaldehyde is generally produced as a 37 per cent solution in water containing a certain amount of methanol impurity. It is a relatively costly operation to purify further and it is not necessary to do so for most of the established end products. Capacities as low as 5,000 tons per year can prove economic, but such a capacity would be based on imported feedstock since it would only consume about 2,200 tons of methanol per year. It is probable that approximately 12,000 tons of formaldehyde per year would be the smallest capacity that could be justified along with a methanol plant unless there was a substantial demand for methanol for other purposes. The production costs to be expected in a developing country are given in table 18. It is assumed that methanol is charged in at the transfer price calculated above.

TABLE 18. PRODUCTION COSTS FOR 37 PER CENT FORMALDEHYDE FROM METHANOL^a

	Costs (cents/lb)
Methanol	1.90
Utilities	0.04
Labour and supervision	0.07
Maintenance, taxes, overheads	0.47
Depreciation	0.36
Total cost of production	2.84
25% return on total capital	0.89
Transfer price	3.73
BLCC investment (millions of US dollars)	0.65

^aThese costs are relevant to a plant with a capacity of 12,000 tons per year.

Polystyrene, styrene-acrylonitrile, acrylonitrile-butadiene-styrene, polyvinyl and methacrylic acid copolymers in a multipurpose thermoplastic resin plant

Several of these polymers have been mentioned above and economic data have been presented for plants in which a separate plant has been assumed for each material produced. It is quite possible, however, that a developing country with a very small initial market will find it attractive to make its initial polymer plant investment in a unit which is capable of producing several polymers on a campaign basis.

Following a general paper exploring this possibility presented at the United Nations Teheran Conference in 1964 (12), Dr. H. L. List of City University of New York and Chem Systems Inc. and Mr. P. H. Spitz of Chem Systems Inc. presented the economic considerations for a particular plant design at the thirty-sixth International Congress of Industrial Chemistry in Brussels in September 1966 (6).

The above discussion on polystyrene included the data on the 2,500 tons per year capacity polystyrene plant in table 10. This is a possible capacity of the multipurpose reactor system, and the figures given are for this plant when making polystyrene alone. In figure 5 the data with respect to unit product cost in a polystyrene plant and the price of styrene monomer are charted. Figure 6 presents three curves representing the investment (a) for various capacity plants for polystyrene alone, (b) for a plant for both polystyrene and ABS resins, and (c) for a plant designed for polyvinyl chloride, ABS and polystyrene. Similar curves, showing

additional investments, could be drawn for each additional product capability which is added. Investments and manufacturing costs will vary with location.

It should be pointed out that the curves in figures 5 and 6 and table 10 are somewhat different from those in the paper presented at the International Congress of Industrial Chemistry. Investment costs have been updated to a 1967 Gulf Coast basis, operating costs are for a specific South American location, and the cost bases, including a 25 per cent return on total capital, have been assumed in order to be consistent with the rest of this report.

This multipurpose system may make excellent economic sense for the proper location. It represents a way for a developing country to enter the important thermoplastic resin field with very low capital investment.

Vinyl acetate

Vinyl acetate monomer is used in three major markets. The monomer is polymerized to polyvinyl acetate which, in turn, is hydrolyzed to polyvinyl alcohol which is then treated with aldehydes to form acetyl derivative.

About half of the monomer is sold as polyvinyl acetate. Its principal use is in paints and coatings, adhesives, and textile resins.

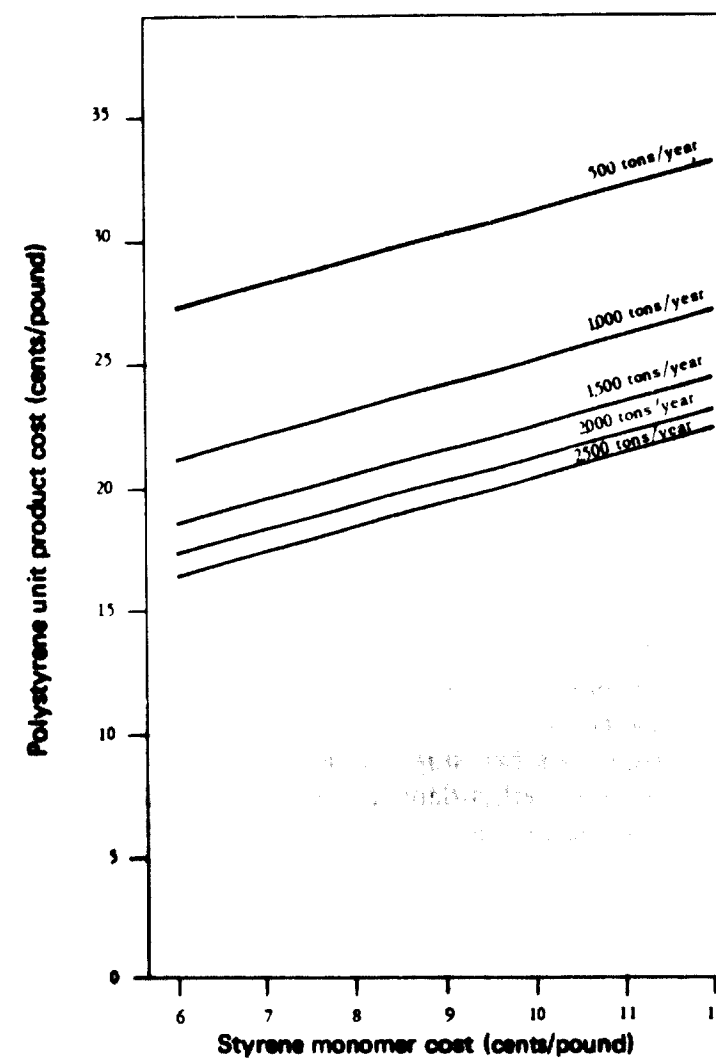


Figure 5. Polystyrene unit product cost versus styrene monomer cost

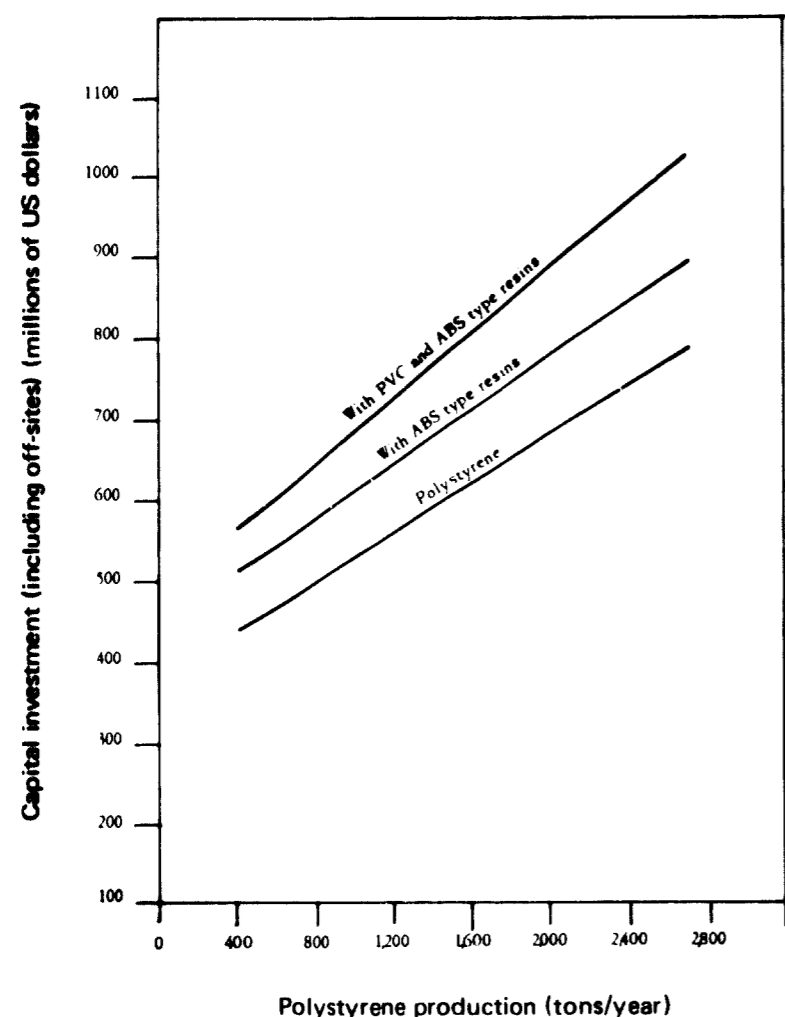


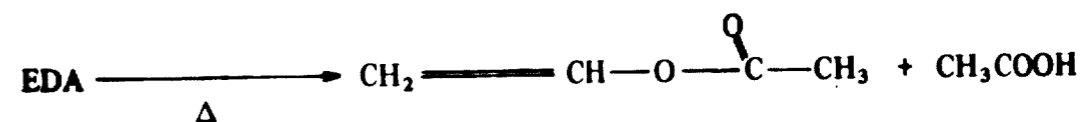
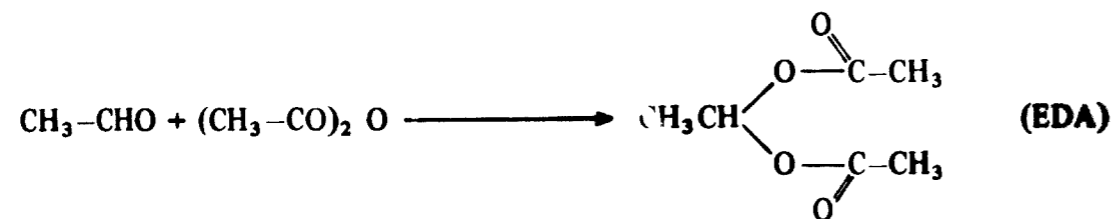
Figure 6. Capital investment versus production

Polyvinyl alcohol is partially or completely hydrolyzed polyvinyl acetate and accounts for about 18 per cent of the consumption of vinyl acetate. The polymer is an effective emulsifying and dispersing agent for vegetable oils, plasticizers, resins and waxes and is used for textile sizing and in adhesive formulations.

The major acetal is polyvinyl butyral which is used as an inner layer in safety glass. This market consumes about 10 per cent of the vinyl acetate produced.

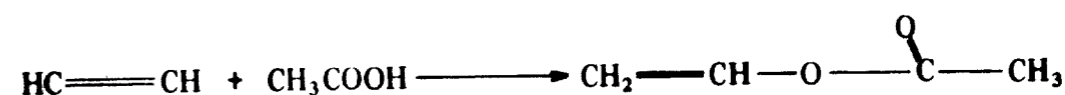
There are three major alternate feedstocks for monomer production: acetaldehyde, acetylene and ethylene.

The acetaldehyde route is a two-stage process which first reacts acetaldehyde with acetic anhydride to form ethylidene diacetate (EDA) and then cracks this material to vinyl acetate and acetic acid:



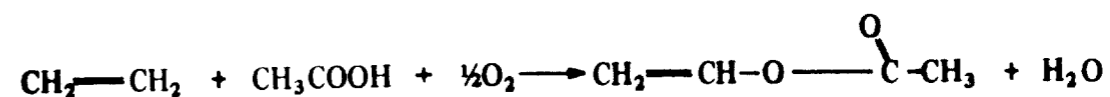
Owing to the large amount of materials which have to be distilled in this process, cheap utilities must be available. There must also be either a market for the appreciable amounts of acetic acid that are formed as a by-product, or the expensive ketene process must be employed for converting acetic acid back to the anhydride. This process is not in competition with the alternate routes and has been used only in special situations. It should not be considered for future plants.

The acetylene-based process reacts the raw materials in the vapour phase over a catalyst to form vinyl acetate directly:



The process is distinguished by high yields, simple operation of the reaction and low catalyst costs. The formation of by-products is very low.

There are two ethylene-based processes, liquid-phase and vapour-phase. In the liquid-phase process, ethylene and oxygen are bubbled through an acetic acid solution containing palladium chloride and copper chloride. Vinyl acetate and co-product acetaldehyde are produced. The amount of acetaldehyde formed is determined by the water content of the acetic acid and is usually significant (at least 1 mole per mole of vinyl acetate):



In an industrial scale process, the total yield of vinyl acetate and acetaldehyde and acetic acid, formed in small amounts by further oxidation of the acetaldehyde, is 90 per cent calculated on ethylene and at least 95 per cent related to the amount of acetic acid used.

The economic considerations of this process compared with the acetylene/vinyl acetate process depend on the difference in price between acetylene and ethylene and also on the size of the plant. Reactors with an annual capacity of 50,000 tons are said to be feasible. The investment costs required are at least 50 per cent higher than in the case of the acetylene process. The consumption of energy is also higher on account of the larger distillation demands.

In the vapour-phase process, the reaction is carried out in such a way that ethylene, acetic acid vapours and oxygen are passed over noble metal catalysts at temperatures of about 160 to 200°C and at a pressure between atmospheric and about 7 atm gauge. The catalyst is generally employed in lumps which are fixed in the reaction chamber. On passing through the reactor, a portion of the reaction participants is converted. After removing the reaction products, the non-reacted material returns to the reactor, supplemented by fresh feed.

In contrast to the liquid-phase process, practically no acetaldehyde is formed here. Other organic by-products are formed only in minor amounts. The reaction proceeds directly towards formation of the desired vinyl acetate. Oxidation of ethylene to carbon oxides is slight. Since no chloride ions are present, no chlorine-containing organic compounds can be formed, a situation which simplifies the corrosion problems.

The economics of the acetylene-based process are relatively insensitive to scale since the raw material costs alone account for more than 85 per cent of the cost of production.

The ethylene-based processes, owing to their higher investment requirements and associated capital charges, are sensitive to scale and should most likely be included within a highly developed complex. For instance, in both the liquid-phase and vapour-phase ethylene processes, oxygen must be available; in the liquid-phase process, the co-product acetaldehyde should be converted to acetic acid. Ethylene-based processes have been built or announced with a minimum size of about 45 million pounds per year and a maximum size of 300 million pounds per year.

With this in mind, it is estimated that even with relatively inexpensive acetylene (7.5 cents per pound), the production costs of a 20 million pound per year acetylene-based vinyl acetate plant would be nearly 25 to 30 per cent higher than those for a moderate-sized ethylene-based unit.

The conclusion drawn is that a new vinyl acetate plant should be based on ethylene feed and its capacity should probably be in excess of 40 million pounds per year in order to be economical. This chemical, therefore, should not be high on the list of priorities of a developing country.

Oxo alcohols

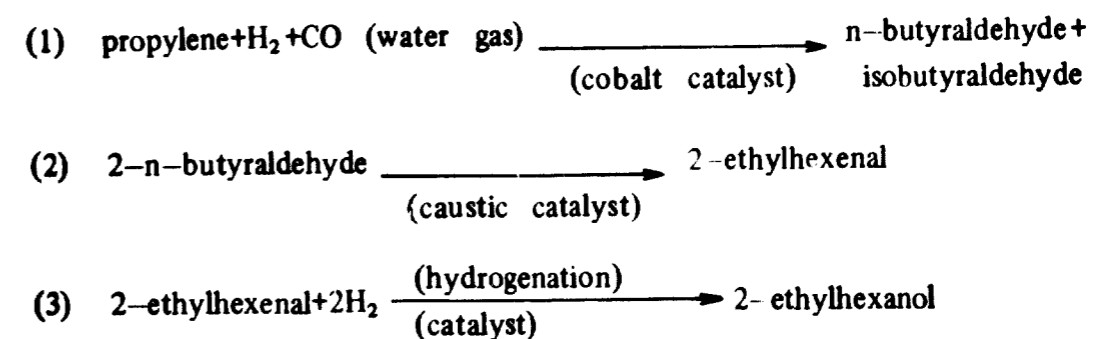
Once vinyl chloride monomer and polymer are being produced within a country, consideration is soon given to producing vinyl plasticizers which make up slightly more than 40 per cent of the finished vinyl product. These plasticizers are produced by the reaction of phthalic anhydride with C_8-C_{10} alcohols. The minimum-sized plant necessary for economic operations in the production of oxo-alcohol is in the capacity range of 10,000 to 15,000 tons per year.

Prior to the development of the oxo processes, the dominant plasticizer alcohol, 2-ethylhexanol, was made *via* aldol condensation. The use of cheap propylene and propylene olefins (heptenes, nonenes) as oxo feedstock via a cheaper route leads to the same or equivalent materials.

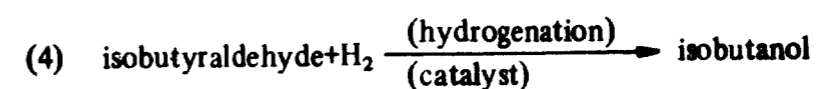
The oxo reaction to produce alcohols from olefins, carbon monoxide and hydrogen was discovered in Germany in 1938 and introduced in the United States in 1948. Many alcohols can be produced by the oxo process (see table 19), but over 70 per cent of those produced are of the C_8-C_{10} range. The product 2-ethylhexanol is made from propylene, isooctyl alcohol from mixed heptenes, and isodecyl alcohol from mixed nonenes.

TABLE 19. PROCESS CHEMISTRY

Product: 2-ethylhexanol

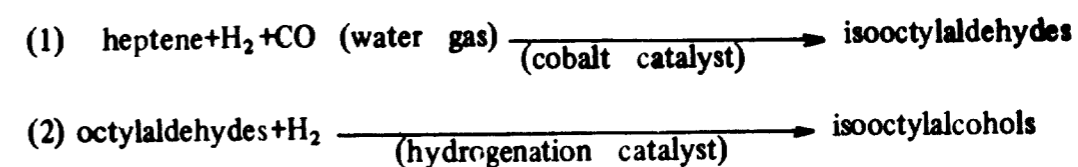


By-product: isobutanol



n-butylaldehyde can also be hydrogenated to n-butanol

Product: isooctanol



The sources and types of oxo alcohol technology used throughout the world are as follows:

Source	Technology
BASF	Propylene-based process to butanols and/or 2-ethylhexanol. Have licensed two plants.
ESSO	Conventional process for heptene and higher olefin feedstocks. Propylene technology is for an Aldox process.
Gulf Oil	Conventional process for heptene and higher olefin feedstocks.
Kuhlman	Conventional process for heptene and higher olefin feedstocks. Have licensed two plants.
Mitsubishi	Propylene-based process to butanols and/or 2-ethylhexanol.
Monsanto/Scientific Design	Conventional process for heptene and higher olefin feedstocks. Aldox type process for propylene feedstocks. Piloted process, not yet licensed.

Montecatini	Propylene-based process to butanols and/or 2-ethylhexanol.
Ruhrchemie/Hoechst-Uhde	Conventional processes for heptene and higher olefin feedstocks. Propylene-based process to butanols and/or 2-ethylhexanol. Five plants in operation or under construction.
Standard of Indiana	Conventional process for olefin and higher olefin feedstocks.
Texas Eastman	Propylene-based process to butanols and/or 2-ethylhexanol.
Union Carbide	Conventional process for heptene and higher olefin feedstocks. Propylene-based process to butanols and/or 2-ethylhexanol.

The type of process selected depends on the local raw material situation. In general, heptenes are unavailable and propylene becomes the logical choice.

There are two types of propylene-based processes available: the conventional route which produces an n-butyraldehyde intermediate which is then processed to 2-ethylhexanol, and the Aldo process which produces both C₄ and C₈ alcohols directly. This latter process produces about 0.45 pounds of C₄ alcohol per pound of C₈ alcohol and its economics depend strongly on the ability to sell C₄ alcohols.

The most promising route, therefore, appears to be a conventional propylene-based process. The propylene feedstock (minimum 92 to 98 per cent propylene depending on the licence, no sulphur, and maximum 0.1 per cent acetylene) is available from most ethylene units and a wide range of feeds can be used for water gas and hydrogen generation. The economic data for this process are presented in table 20.

TABLE 20. PRODUCTION COSTS FOR 2-ETHYLHEXANOL FROM PROPYLENE^a

	Costs (cents/lb)
Raw materials ^b	6.1
Utilities	1.3
Labour and supervision	0.7
Maintenance taxes and overheads	1.7
Depreciation	1.3
By-product credit ^c	(1.9)
Total cost of production	9.2
25 % return on BLCC capital	3.2
Transfer price	12.4

Table 20 (continued)

	Costs (cents/lb)
BLCC investment (millions of US dollars)	3.8

^aThese costs are relevant to a plant with a capacity of 15,000 tons per year.

^bAssumes water gas and hydrogen fed to the oxo unit.

^cFuel values and 0.316 isobutanol per pound 2-ethylhexanol.

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