Chapter 5

Petrochemicals

Just a few years back, it was easy to define petrochemicals—they were relatively pure, identifiable substances derived from petroleum and used in the chemical trade. Now conversion processes are often built in as part of separation processes making original products more complex; oil companies are entering the chemical business; chemical companies are entering the oil business; and the whole group is expanding greatly, so most organic chemical substances could be considered petrochemicals.

Most processes for separating individual species from petroleum involve using refined engineering methods, with distillation and selective adsorption the most important. Once separated, however, most materials then undergo chemical conversion into more desirable products. Alkylations involving propenes and butenes yield C_6 to C_8 hydrocarbons for high-octane gasoline. Propylene becomes polypropylene, propylamines, or propylene glycol and ethers. Every phase of organic chemistry has been touched and altered by the availability of petrochemicals. Even the field of aromatics, once the sole province of coal-derived chemicals, now derives over 98 percent of its raw materials from petroleum. The major production plants developed along the Gulf of Mexico coast, because the needed raw materials and water transport are there, but increasingly plants are spreading out into consuming areas. In addition to the usual organics, by-product sulfur has become a dominant factor in the market.

Oil companies have traditionally made their profits more from production than from product sales. Their thinking has been geared to high-sales low-profit operations in the refining business. There has also been great reluctance to make long-term commitments. This, of course, is the direct opposite of the chemical industry's usual long-time commitments to comparatively low-volume high-profit operations. The growth of the enormous plastic industries and other very large scale organic chemicals (ethylene glycol, methanol, ethanolamines, etc.) has brought the viewpoints of the two industries much closer together. At first, chemical companies bought simple raw materials of the required purity directly from the oil companies; then oil and chemical companies formed joint ventures; now integration from underground oil to finished product is taking place with both oil and chemical companies becoming indistinguishable. Most major oil companies now have petrochemical departments which are frequently separate from their refining departments. The manufacture of intermediates is frequently more profitable than simple raw material supply.

HISTORICAL. The first organic chemical made on a large scale from a petroleum base was isopropyl alcohol (isopropanol), first produced by Standard Oil of New Jersey in 1920. Depending on the definition and the number of conversions permitted by the statistician, certainly over 3000 individual petrochemicals enter into commerce. Over one hundred are presented in this chapter and other parts of the book. This business changes very rapidly as new processes simplify old ones and price changes make usability vary; so many historically important processes have become economically or technologically obsolete. Within the past

few decades, processes for making ammonia, ethyl alcohol, acetic acid, acetone, glycerin, acetylene, and other major chemicals have been revised and are now almost totally petroleum-derived.

RESEARCH. The birth and growth of petrochemicals has been one of the fabulous stories connected with modern chemical and chemical engineering research. Petroleum companies were uninterested in chemical production, but gave the industry a great boost by selling their off-gas to chemical companies at its fuel value. Cracking furnaces put reactive olefins in these gases, which chemical companies quickly developed into petrochemicals. Some oil companies, for example, Shell and Standard Oil of New Jersey (now Exxon), became involved in chemical production much earlier than others.

ECONOMICS AND USES. By 1925, Standard Oil of New Jersey was making 75 t/year of isopropyl alcohol, and the emergence of the petrochemical industry was established in many minds.[1] Currently, well over 80 percent of all organic chemicals are petrochemicals. The percentage continues to increase despite a nearly ten to one increase in the price of raw material. The classes of end use for petrochemical products are listed in Table 38.1. Companies continue to expend large sums on capital improvements needed for petrochemicals, although the industry is currently having a severe sales slump. Prescott[1a] has estimated and tabulated the petrochemical growth of oil and chemical companies since 1974. He predicts a large and profitable growth of the industry, particularly in polymers and agrichemicals. Like other businesses, growth has been delayed by the current recession. Hatch and Matar[2] have made an excellent summary of the technology of the industry.

FEEDSTOCKS. The most basic raw materials (Table 38.2) supplied by petroleum refineries or natural gas companies are LPG, natural gas, gas from cracking operations, liquid distillate (C_4 to C_6), distillate from special cracking processes, and selected or isomerized cyclic fractions for aromatics. Most of these substances are of high value for fuel use, and attention is

[1] t = 1000 kg.

[1a] Prescott, Oil Giants Gear Up Petrochemicals Capacity, *Chem. Eng.* 82 (7) 56 (1975).

[2] Hatch and Matar, *From Hydrocarbons to Petrochemicals*, Gulf, Houston Tex, 1981.

Table 38.1 End Products of the Petrochemical Industry with Reference Chapter Number

Product	Chap.	Product	Chap.
Adhesives	25	Industrial gases	7
Agrichemicals	26	Lubricants and additives	37
Alcohols	38	Medicinal products	40
Ammonia	18	Nitrogen industries	18
Antifreeze and antiknock	38	Paints, varnishes, etc.	25
Detergents	29	Plastics, polymers, and plasticizers	34
Dyes, lakes, and toners	39	Rubber, rubber chemicals	36
Explosives	22	Solvents	38
Fertilizers and pesticides	26	Sulfur and sulfuric acid	19
Flavors and perfumes	27	Surface coatings	24
Flotation agents	38	Synthetic fibers	35
Food additives	26	Synthetic motor fuels	37
Industrial carbon	8		

Table 38.2 Primary Precursors: Petroleum-Petrochemical Complex

Raw Materials by Distillation	Precursors (basic chemicals) by Conversion	Intermediates by Conversion	Finished Products by Conversion
Paraffins and cyclics	Olefins, diolefins, acetylene, aromatics	Various inorganics and organics	Inorganics and organics
Natural gas			Carbon black
Sulfides	H_2S	S, H_2S	H_2SO_4
Hydrogen		Synthesis gas	NH_3
Methane			Methanol
			Formaldehyde
Refinery gases	Acetylene	Acetic acid	Acetates
	Isobutene	Acetic anhydride	Fibers
Ethane°	Ethylene	Isoprene	Rubber
Propane°	Propylene	Ethylene oxide, etc.	Rubber and fiber
n-Butane°	*n*-Butenes	Butadiene	Rubber
Hexane			
Heptanes			
Refinery naphthas			
Naphthenes	Cyclopentadiene	Adipic acid	Fibers
Benzene	Toluene	Ethylbenzene	Styrene
		Styrene	Rubber
		Cumene	Phenol, acetone
		Alkylbenzene	
		Cyclohexane	Nylons
Toluene	Toluene	Phenol	Plastics
		Benzoic acid	Phenol
Xylenes	*o*-, *m*-, *p*-Xylene, toluene	Phthalic anhydride	Plastics
Methyl naphthanes	Naphthalene		

°From LPG and refinery cracked gas.

NOTE: Aromatics are also obtained by chemical conversions (demethylation, etc.).

increasingly turning to the use of less desirable high-molecular-weight feedstocks. To make this source attractive, cost must be less than or the same as the present sources of the low-molecular-weight precursors produced. Coking processes, hydrocracking, and high severity catalytic cracking appear to be the more attractive routes to explore.

Mixtures are usually separated into their components at the petroleum refineries, then chemically converted into reactive precursors before being sold to outside processors or converted into salable chemicals within the plant.

The lower members of the paraffin and olefin series have been the preferred and most economical sources of organic raw material for conversion, so figures and tables are shown concerning the derivations from methane (Fig. 38.1 and Table 38.3), ethylene (Fig. 38.2 and Table 38.4), propylene and butylene (Fig. 38.3 and Table 38.5), and cyclic materials (Fig. 38.4 and Table 38.6). The tonnage of these materials used has increased rapidly for some years, and the number of final products produced has also grown. Presumably, rapid growth will resume as the business climate improves. The manufacture of olefins and aromatics is discussed in Chap. 37 along with some intermediates. Salable products made from these are listed in the various tables and figures of this chapter. The manufacturing procedures for a number of technically important petrochemicals are used to clarify the types of conversion processes discussed in the latter part of the chapter.

As synthetic organic chemistry made new products possible, petrochemicals stood ready to fulfill the demand for raw materials because oil, and particularly natural gas, was available

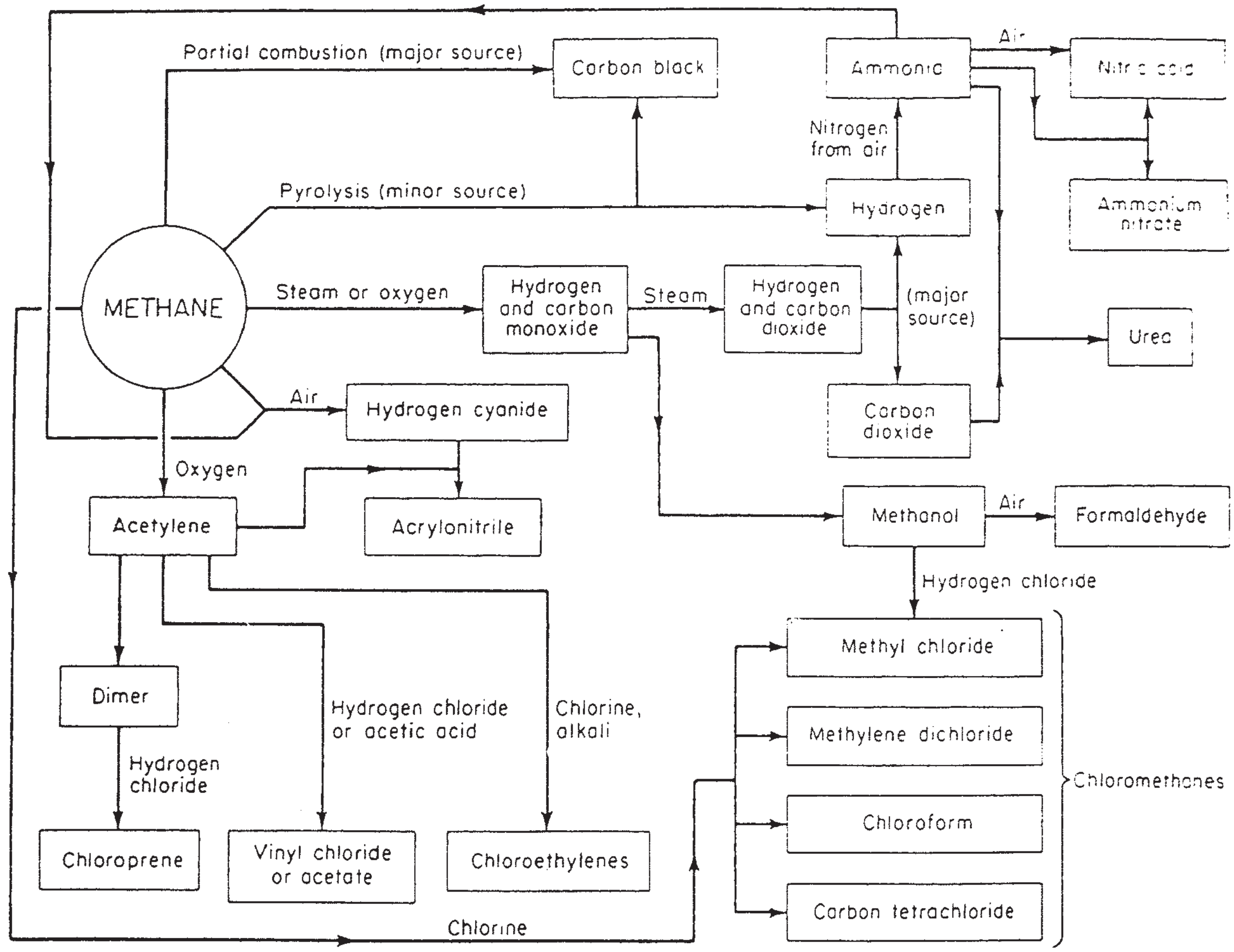

Fig. 38.1. Petrochemicals from methane. *(McGraw-Hill Encyclopedia of Science and Technology, 5th ed., vol. 10, 1982, p. 62.)*

Table 38.3 Petrochemicals from Methane

Basic Derivative	Produced Annually, 10^6 kg (last year reported)*	Uses, percent
Ammonia	17,545	Fertilizer 80, plastics and fibers 10, explosives 5
Carbon black	1,227	Tires 65, other rubber 25, colorant and filler 10
Methanol	3,830	Polymers 50, solvents 10, derivatives (HCHO, CH_3COOH)
Chloromethanes		
CH_3Cl, methyl chloride	177	Silicones 57, tetramethyl lead 19
CH_2Cl_2, methylene chloride	236	Paint remover 30, aerosol propellant 20, degreaser 10
$CHCl_3$, chloroform	183	Fluorocarbons 90
CCl_4, carbon tetrachloride	322	Fluorocarbons 95, degreasing, fumigant, etc. 5
Acetylene	131	VCM 37, 1,4-butanediol 25, V acetate 14, V fluoride, and acetylene black 5
Hydrogen cyanide	227	MMA 58, cyanuric chloride 17, chelating agents 13, NaCN 9

*Usually 1981.

SOURCES: *Chem. Eng. News* and *Chem. Mark. Rep.*

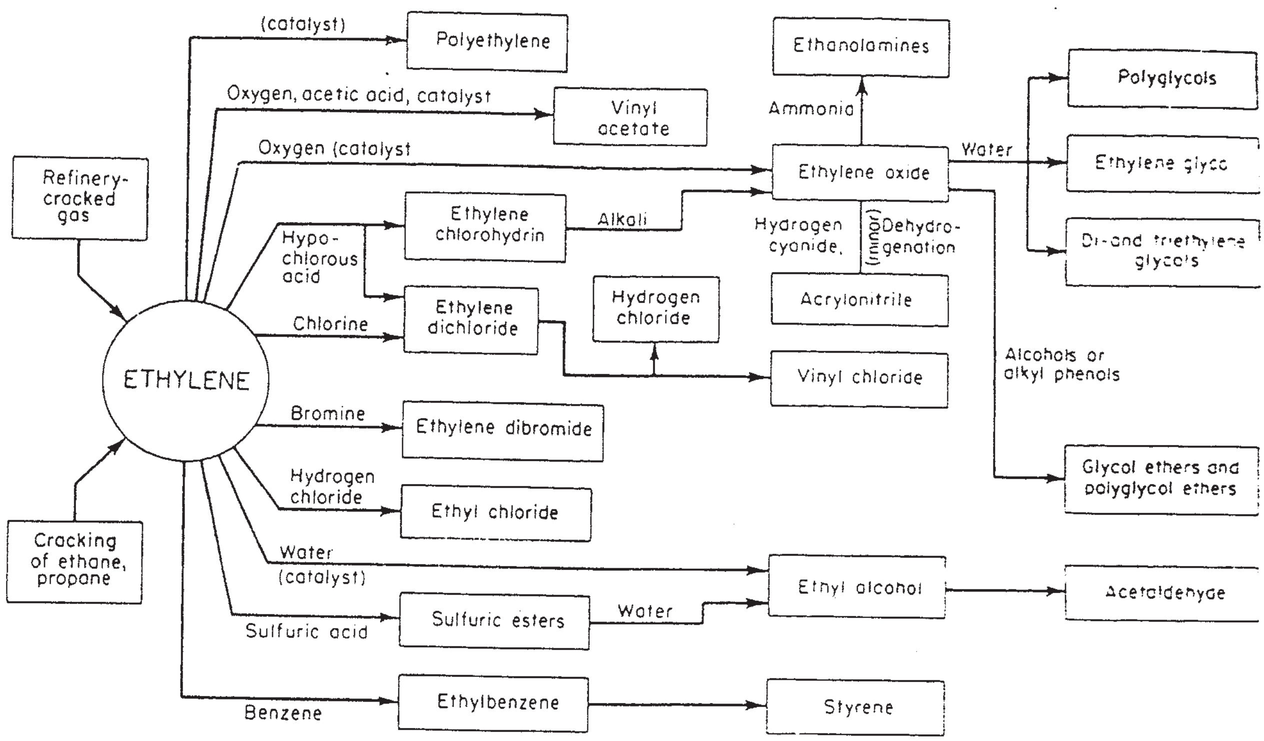

Fig. 38.2. Petrochemicals from ethylene. *(McGraw-Hill Encyclopedia of Science and Technology, 5th ed., vol. 10, 1982, p. 63.)*

Table 38.4 Petrochemicals from Ethylene

Basic Derivative	Produced Annually, 10^6 kg (last year reported)°	Uses, percent
Ethyl benzene	3474	Styrene 99, solvent 1
Ethyl chloride	191	TEL 90, ethyl cellulose and pharmaceuticals 5
Ethylene dichloride	5227	VCM 84, solvent 7
Ethylene glycol	2050	Antifreeze 38, polyester fibers and films 49
Ethylene oxide	2320	Glycol 60, ethoxylates 10, glycol ethers 10
Perchloroethylene	327	Textile cleaning 40, metal cleaning 21, chemical intermediate 6
Polyethylene		
Low density (including LLDPE)	3320	Film, sheet, molding, and extrusion plastic
High density	2186	Film, sheet, molding, and extrusion plastic
Styrene	3182	Polystyrene 52, ABS 9, SBR 7, polyester resins 6, SB latex 6
1,1,1-Trichloroethane	283	Cold cleaning 40, vapor degreasing 22, adhesives 12, aerosols 10, electronics 6

°Usually 1981.

SOURCE: *Chem. Eng. News* and *Chem. Mark. Rep.*

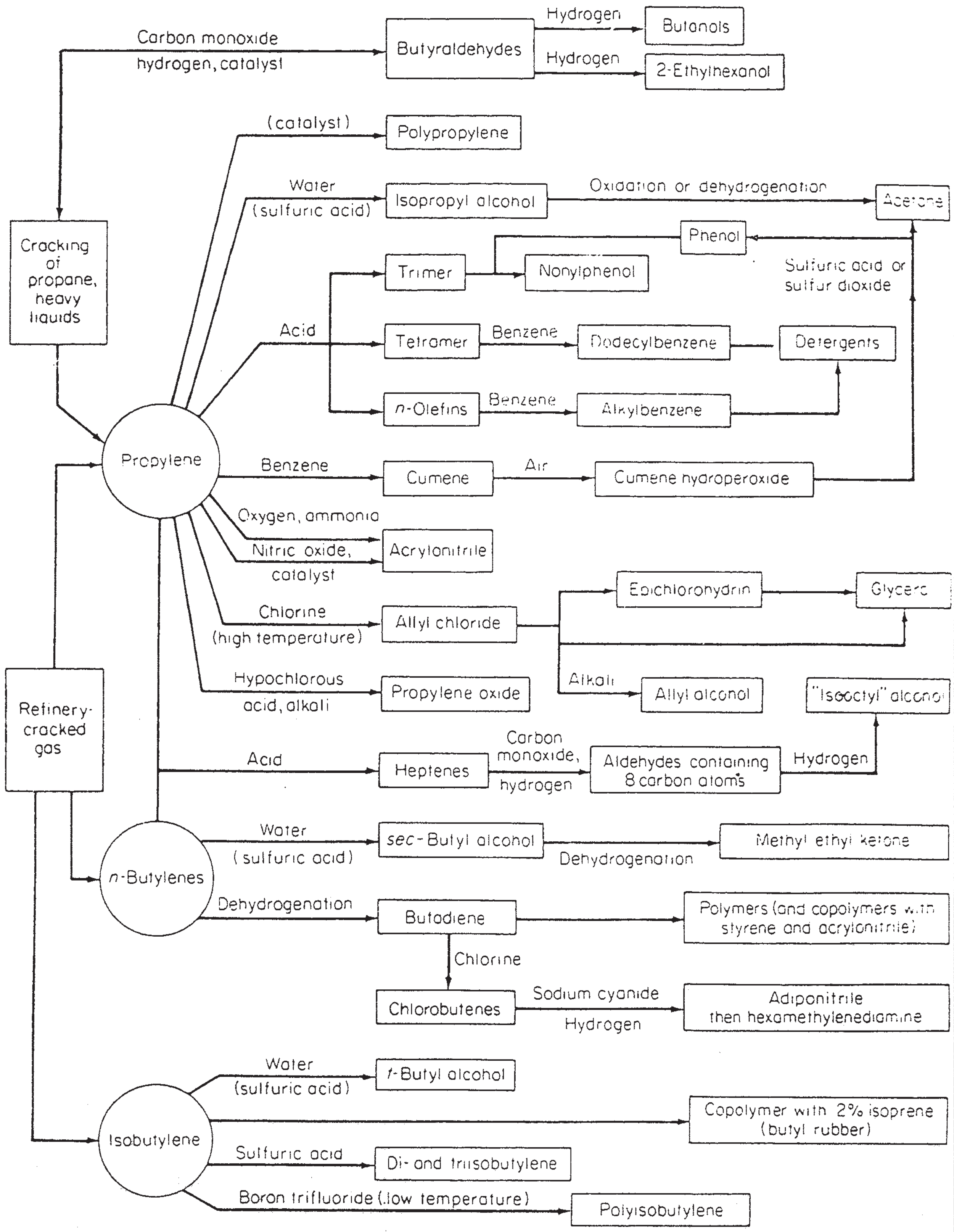

Fig. 38.3. Petrochemicals from propylene and the butylenes. *(McGraw-Hill Encyclopedia of Science and Technology, vol. 10, 1982, p. 65.)*

Table 38.5 Petrochemicals from Propylene and the Butylenes

Basic Derivative	Produced Annually, 10^6 kg (last year reported)°	Uses, percent
Acrylonitrile	327	Apparel 70, home furnishings 30
Butadiene	909	SBR 40, polybutadiene 20, hexamethylenediamine 10
n-Butanol	341	Acrylates 30, glycol ethers 22, butyl acetate 12, solvent 11, plasticizers 9, amino resins 7
Butyl rubber	409	Tires, high-impact resins
Cumene	1864	Phenol and acetone 98
Dodecene (propylene tetramer)	120	Detergents, dodecyl sulfonate
Isopropyl alcohol	845	Acetone 43, process solvent 10, coating solvent 10, pharmaceutical and cosmetics 6
Nonene (propylene trimer)	162	Polyglycol ethers
Oxo alcohols (2-ethyl hexanol)	182	Plasticizers 65, acrylate esters 15
Polypropylene	1864	Injection molding 30, fibers and filaments 26, extrusion 11
Propylene oxide	818	Urethane polyols 54, propylene glycol 21, amines and ethers 13

°Usually 1981.

SOURCES: *Chem. Eng. News* and *Chem. Mark. Rep.*

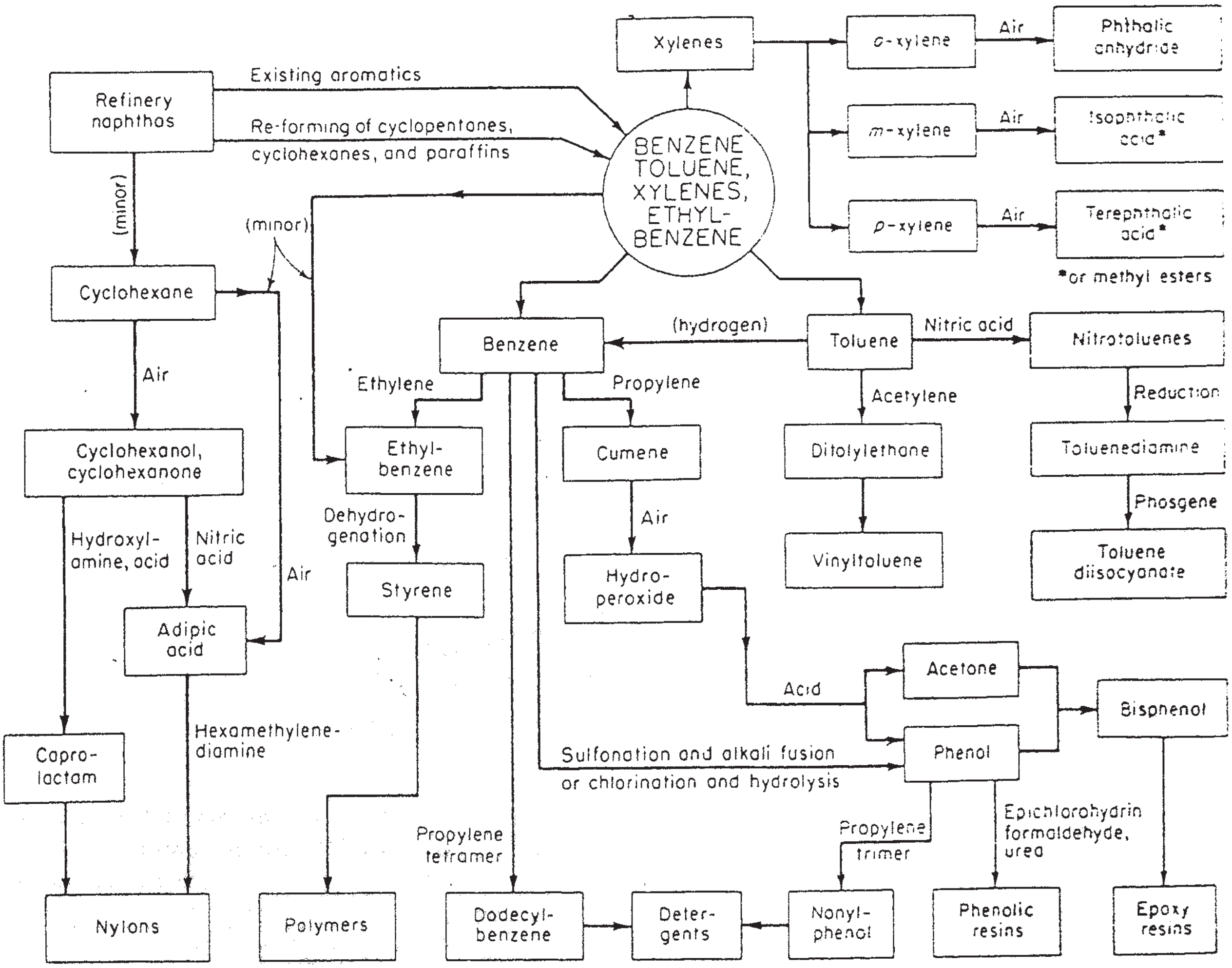

Fig. 38.4. Cyclic petrochemicals. *(McGraw-Hill Encyclopedia of Science and Technology, 5th ed., vol. 10, 1982, p. 67.)*

Table 38.6 Cyclic Petrochemicals

Basic Derivative	Produced Annually, 10^6 kg (last year reported)*	Uses, percent
Benzene	5285	Ethylbenzene 49, cumene 18, cyclohexane 15, nitrobenzene/aniline 5
Cyclohexane	682	Adipic acid 60, caprolactam 30
Ethylbenzene	3500	Styrene 99
Toluene	3339	Octane improver, benzene, xylene
Xylenes		
p-Xylene	1864	Dimethylterephthalate and terephthalic acid 100
o-Xylene	455	Phthalic anhydride
m-Xylene	n.a.†	Octane improver

*Usually 1981.
†n.a., not available
SOURCES: *Chem. Eng. News* and *Chem. Mark. Rep.*

in assured supply at very modest cost, in part due to chemical engineering advancement in effective separation processes. Research in conversion processes enabled low-valued molecules to be converted into more valuable ones. From these substances comes an almost unlimited supply of raw materials for expanding industry: antifreeze, lube oil additives, resins for plastics, synthetic fibers, and protective coatings.

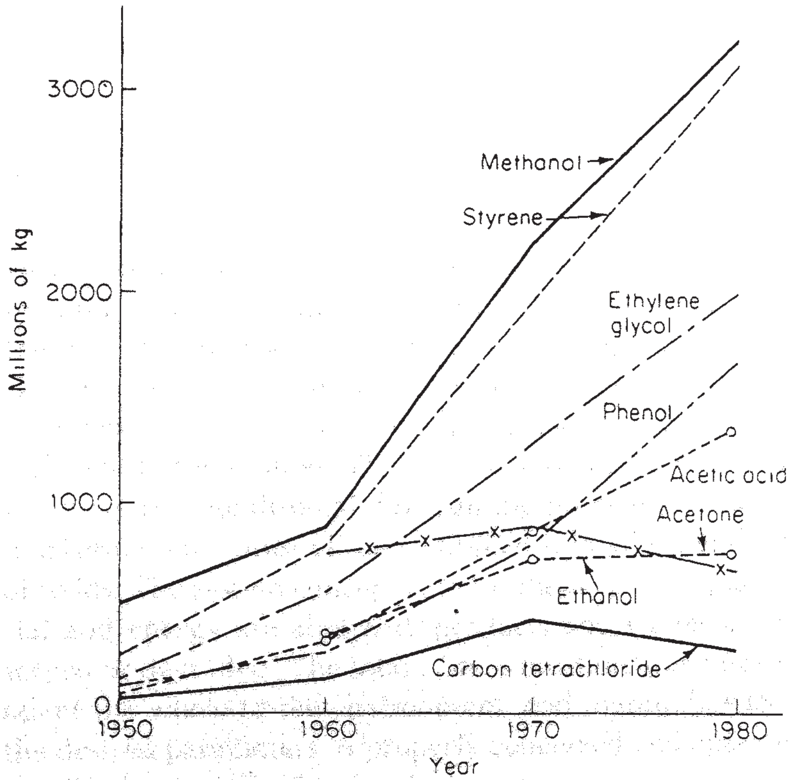

Fig. 38.5. Growth and production of important petrochemicals in the United States. *(United States International Trade Commission.)*

UNIT OPERATIONS (or Physical Separation Methods)

New understanding of the parameters affecting separative processes and the application of mathematics to such work enables better separations with lower energy consumption. The availability of adequate theory concerning such processes and the emergence of computer technology to make calculation and modeling less onerous has opened up whole new fields for work. The major unit operations that have been used are listed in Table 37.5 and are described in Chap. 37.

TRANSPORTATION. It is not generally recognized, but there are many miles of pipelines carrying such materials as ammonia and ethylene over considerable distances at low cost. The other low-cost transportation methods are ships, barges, and of course railways and trucks are used for smaller quantities.

CHEMICAL CONVERSIONS

Early years saw emphasis on a constantly increasing number of new products. As new product uses spread, many competed with one another for increasingly scarce feedstocks. More stress is now being laid upon new and cheaper methods of production than on new products. Many new reactions are more complicated and novel. Most new processes are continuous, and extensive use is made of instruments for analysis and control. Computer control has proved to be highly successful.

MANUFACTURE OF PETROCHEMICALS

Novel and efficient methods of manufacturing petrochemicals continue to be devised by the research and development departments of the various companies. It is convenient to examine these on the orderly basis of the chemical conversion types. Although rather old, the book by Groggins[3] is most useful in understanding these unit processes.

Discovering a suitable economical method to manage a known chemical reaction is not sufficient in these times. The control of quality, environmental effects of the product and by-products, sewage disposal, fire fighting procedures, start-up problems, safety, packaging and marketing, etc., must all be combined into a "system" utilizing professionals from a variety of fields. The system concept extends the scope of a plant beyond just processing where material and energy are absorbed, products and wastes are removed, and energy is either conserved or degraded. The total system must include information processing to sell and service, adapt the whole to the environment, and manipulate the summed information to maximize the desired parameters. A properly conceived and operated system offers no problems to society. Production of petrochemicals is enormous compared with other chemicals (over 2×10^9 kg/year for ethylene alone) as illustrated by the figures and tables, particularly Fig. 38.5.

[3]Groggins (ed.), *Unit Processes in Organic Syntheses*, 5th ed., McGraw-Hill, New York, 1958.

Probably the most notable new developments are the extensive use of selective catalysts to effect increased reaction rates and the improved recovery of heat that was formerly wasted because fuel was very cheap.

ALKYLATION, DEALKYLATION, AND HYDRODEALKYLATION.[4] The largest volume chemical alkylations are certainly benzene by ethylene to form ethylbenzene on the way to becoming styrene, discussed in Chap. 36; linear alkyl benzene for manufacturing detergents discussed in Chap. 26; and the benzene-propylene alkylation to form cumene from which phenol and acetone are derived. The alkylation of lead to form tetraethyl and tetramethyl lead is of diminishing importance as lead is phased out as a gasoline additive. The production of alkylated gasoline is larger than any of these, but the formed alkylates are not isolated and the products obtained are rarely considered to be chemical entities. Alkylation of gasoline is discussed in Chap. 37.

Cumene[5] is isopropyl benzene and is made by reacting benzene with propylene over a catalyst such as a phosphoric acid derivative at 250°C and 700 kPa. A refinery cut of mixed propylene-propane is frequently used instead of the more expensive pure propylene. Benzene is provided in substantial excess to avoid polyalkylation. Other catalysts which have been used are aluminum chloride and sulfuric acid.

Ethylbenzene[6] is made from benzene and ethylene using several modifications of the older mixed liquid-gas reaction system using aluminum chloride as a catalyst. One catalyst is proprietary, but not so corrosive as the usual Friedel-Craft catalysts. The reaction takes place in the gas phase over a fixed bed unit at 370°C under a pressure of 1450 to 2850 kPa. Unchanged and polyethylated materials are recirculated making a yield of 98 percent possible. The catalyst operates several days before requiring regeneration.

Dealkylation and hydrodealkylation are now practiced quite extensively to convert available molecules into others more desired. Two such processes practiced extensively are:

1. Toluene or xylene or C_9 and heavier aromatics + H_2 (presence of a dealkylation catalyst) = mainly benzene.
2. 2 toluene + a little H_2 (presence of a fixed bed catalyst) = benzene + mixed xylenes

Tetraethyl lead is prepared commercially by two processes. The first and older process involves the reaction between ethyl chloride and a sodium-lead alloy:

$$4PbNa + 4C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl$$

A newer electrolytic process[7] uses the Grignard reagent and an electrolytic cell to produce either TEL or TML:

$$2RMgCl + 2RCl + Pb \xrightarrow[\text{current}]{\text{electric}} PbR_4 + 2MgCl_2$$

[4]Groggins, op. cit., p. 804; Sittig, *Aromatic Hydrocarbons*, Noyes, Park Ridge, N.J., 1976.

[5]Albright, Alkylation Processes, HF as a Catalyst, *Chem. Eng.* 73 (19) 205 (1966); Matox, *Trans. AIChE* 41 463 (1945).

[6]Dwyer, Lewis, and Schneider, Efficient, Non-polluting Ethylbenzene Process, *Chem. Eng.* 83 (1) 90 (1976).

[7]*Chem. Eng.* 72 (13) 102 (1965); 72 (23) 249 (1965); Electrolytic TEL, *Chem. Week* 94 (24) 77 (1964); Hard Hit Antiknocks Still Generate Cash, *Chem. Week* 132 (3) 50 (1983).