

PRODUCTS OF REFINING

Precursors of Petrochemicals

As markets change, there is constant alteration in the materials used for the manufacture of petrochemicals. Almost any synthesis desired can be brought about; the problem is to do it at low cost with the equipment available. Table 37.5 shows the unit operations involved. In earlier times, acetylene was used extensively for making petrochemicals, but it is difficult to make and store, so ethylene has now become the principal raw material for further synthesis.¹⁹ Precursors are reactive materials usually made by breaking down larger molecules, called feedstocks. Ethylene is currently being made from LNG, naphtha, gas oil, diesel fuel, ethane, propane, and butane, with coal a possibility soon to be explored, and some testing of liquefied coal already completed. The principal precursors are:

Acetylene	Propylene	Benzene	Xylenes
Ethylene	Butene	Toluene	Naphthalene

Acetylene production is covered in Chap. 7.

The manufacture of *ethylene* from distillates, natural gas, or gas liquids is shown in the generalized flowchart of Fig. 37.4. This is the largest volume organic material. The conditions for its manufacture lie somewhere between those usually thought of as refining and those encountered in chemical production. Extremely large plants are built and being built. Some plants have a production capacity as large as 7×10^8 kg/year. In 1980, 57 percent of ethylene

¹⁹Kniel, Winter, and Stork, *Ethylene—Keystone to the Petrochemical Industry*, Marcel Dekker, New York, 1980; Brumm, How Will They Feed the Ethylene Plants of the 1990's? *Chem. Bus.*, October 20, 1980, p. 19.

Table 37.5 Unit Operations for Separation of Olefins and Aromatics as Precursors of Petrochemicals

Operation	Based on Differences In:	Product
<i>Vapor-Liquid</i>		
Distillation	Vapor pressure	Ethylene from ethane
Extractive distillation	Polarizability	<i>n</i> -Butenes from butanes
Azeotropic distillation	Polarizability	Toluene from aromatics
Absorption	Solubility	Ethane from methane
<i>Liquid-Liquid</i>		
Solvent extraction	Solubility	Benzene from aliphatics
<i>Liquid-Solid</i>		
Crystallization	Melting point	<i>p</i> -from other xylene
Extractive crystallization	Clathrate* formation	<i>n</i> -Paraffins from other hydrocarbons
Encapsulation	Clathrate formation	<i>m</i> -Xylene
Adsorption on molecular sieves	Surface or pore adsorption	<i>n</i> -Paraffins from isoparaffins
<i>Vapor-Solid</i>		
Adsorption on molecular sieves	Surface or pore adsorption	Ethylene from ethane

* Clathrates separate primarily on molecular size and shape.

NOTE: In addition to the physical property differentials tabulated here, chemical differentials are employed, e.g., reversible chemical reaction rates or chemical equilibria, as exemplified by separating pure butadiene from butene, using reaction with cuprous salts.

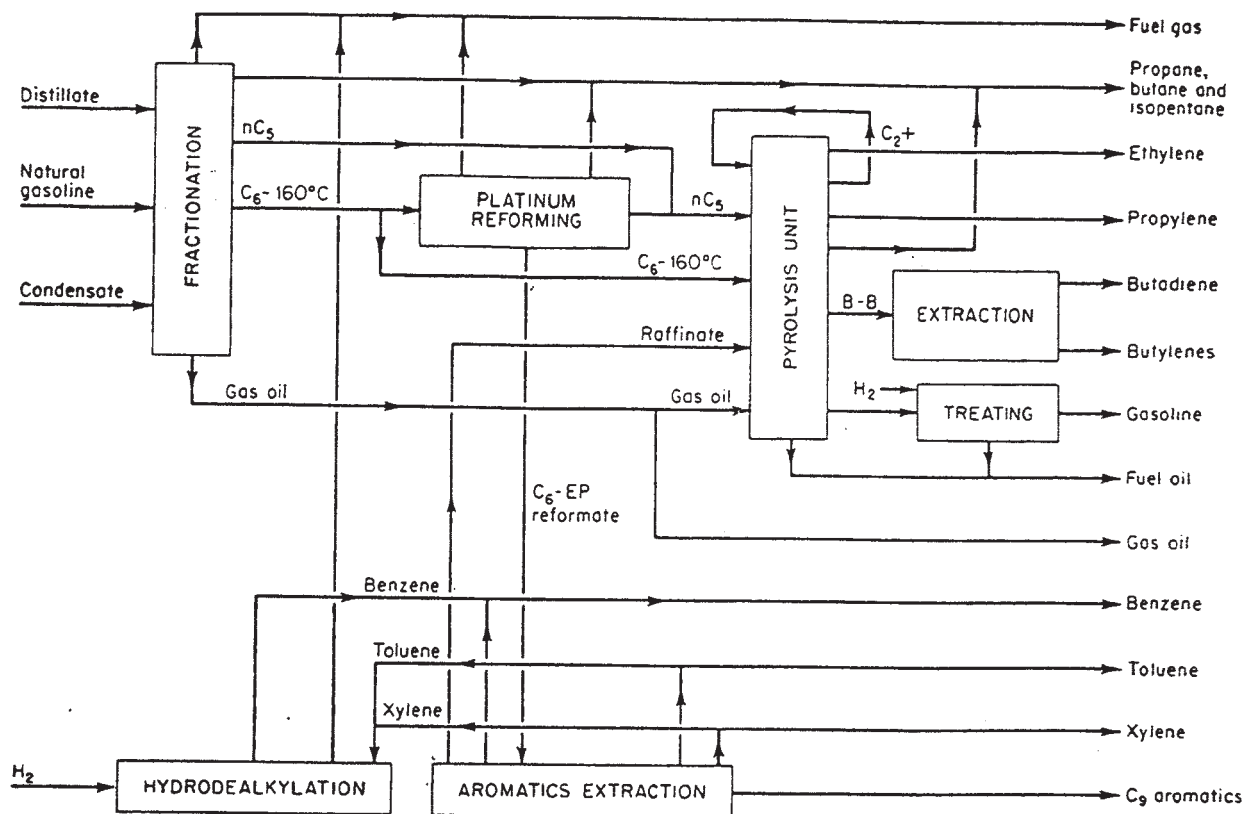


Fig. 37.4. Generalized flowchart for the production of petrochemicals. (M. W. Kellogg Co.)

production was based on NGLs; by 1990 the feed is expected to be 60% light hydrocarbons and 40% refinery products.²⁰ The material to be processed (cracked) is diluted with an inert gas (usually steam) at around 925°C with a residence time of 30 to 100 ms which yields a mixed product which must be separated to be useful. The gases are rapidly quenched, chilled, dehydrated, and fractionated to yield high-purity individual components and unwanted material for recycling. Changing feedstocks and conditions alter the product composition, e.g., butylene or propylene could be made the primary product, if desired. The flowchart of Fig. 37.5 shows the manufacture from refinery gas with the analysis (in percent): methane,

²⁰Kniel, op. cit.

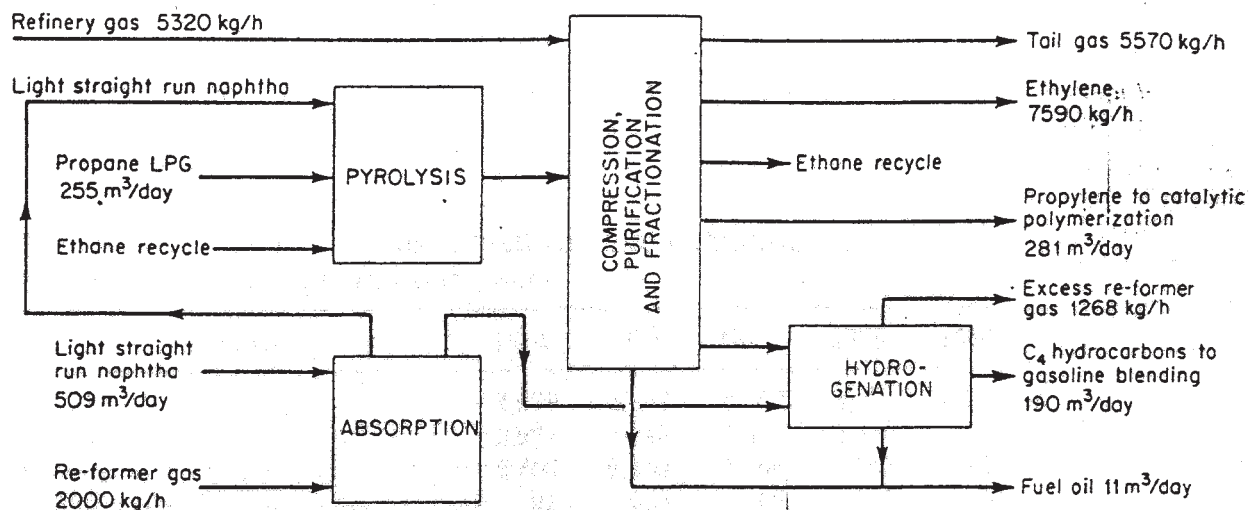


Fig. 37.5. Flowchart for ethylene and propylene production from refinery gas. (Chem. Eng. and M. W. Kellogg Co.)

25; hydrogen, 19; ethane, 15; ethylene, 7; propane, 12; and propylene, 6, with the remainder N_2 , CO , CO_2 , H_2S , and higher hydrocarbons. LPG, high-run gasoline, and ethylene recycle may be added to this. Ethylene production in 1982 was 13.6×10^9 kg/year, but plant capacity was 18.6×10^9 kg/year. Much of the idle capacity was designed for naphtha or gas oil feed, which have become more expensive than light hydrocarbons as a source of ethylene.

A high-severity short-time crack of naphtha feedstock yielded²¹ a mix containing (in percent): hydrogen, 1.2; methane, 15.2; acetylene, 1.3; ethylene, 31.8; ethane, 1.2; propadiene, 1.2; propylene, 11.6; propane, 0.3; butadiene, 4.7; butylene, 2.2; and C_{5+} liquids, 27.7.

The increasing cost of light feedstocks and the demand for naphthas for other uses have caused increasing attention²² to be paid to heavier fractions such as vacuum gas oils, which have become a glut on the market. Both in the United States and abroad, extensive experiments have shown that the production of olefins from such heavy feedstocks, even heavy crude, is possible and will take place when economic conditions warrant it.

Propylene²³ is rarely produced except as a coproduct with ethylene. Steam cracking of ethylene produces most of it, and virtually all of it is used for polymer production. The remainder, used mostly for chemical production, comes from oil refinery fluid catalytic crackers. Refinery propylene is used mainly for alkylation. Production in 1982 was 7.3×10^9 kg/year with a plant capacity of 10.4×10^9 kg/year.

Aromatics are usually thought of as coal-derived, but the amount from that source in 1980 was almost vanishingly small, 4 percent of the benzene, 0.9 percent of the toluene, and only 0.1 percent of the xylenes. Table 37.6 gives statistics for U.S. production, and Fig. 37.6 shows the interrelation between uses and sources. Benzene can be made by *dehydrogenation* of cyclohexane or substituted cyclohexanes, by *aromatization* of methylcyclopentane, and by *demethylation* of toluene or xylenes. The demand for aromatics is large and attention is being given to find catalysts to produce more BTX (benzene-toluene-xylene) for chemical and high-grade fuel use. Toluene is recoverable, as such, from a few stocks, but most is made by dehydrogenation of naphtha; e.g., methylcyclohexane is dehydrogenated to toluene. This can then be demethylated to benzene, if desired.

Naphthalene is used in smaller quantities than the lighter aromatics, but with 2×10^7 kg used in 1981, its consumption is far from trivial. Six U.S. plants have a combined capacity of

²¹Prescott, Pyrolysis Furnace Boosts the Ethylene Yield by 10–20%, *Chem. Eng.* 82 (14) 52 (1975).

²²Baldwin and Kamm, ACR Process for Ethylene, *Chem. Eng. Prog.* 79 (1) 68 (1983); Fujita et al., Olefins from Heavy Oils, *Chem. Eng. Prog.* 79 (1) 76 (1983).

²³Spitz, Propylene—Key Question of the Future, *Chem. Eng. Prog.* 71 (11) 13 (1976).

Table 37.6 U.S. Petroleum-Based Aromatic Production
(in millions of kilograms per year)

Product	1974	1976	1977	1978	1980
Benzene	4,679	4,467	4,562	4,774	6,510
Toluene	2,977	3,245	3,317	3,428	3,308
Xylenes	2,760	2,489	2,796	2,915	3,134
Naphthalene	91	255	69	71	46
Other aromatics and naphthenes	1,551	1,991	1,434	1,874	1,815
Grand total	12,058	12,447	12,178	13,062	14,813

From data of the U.S. International Trade Commission, annually.

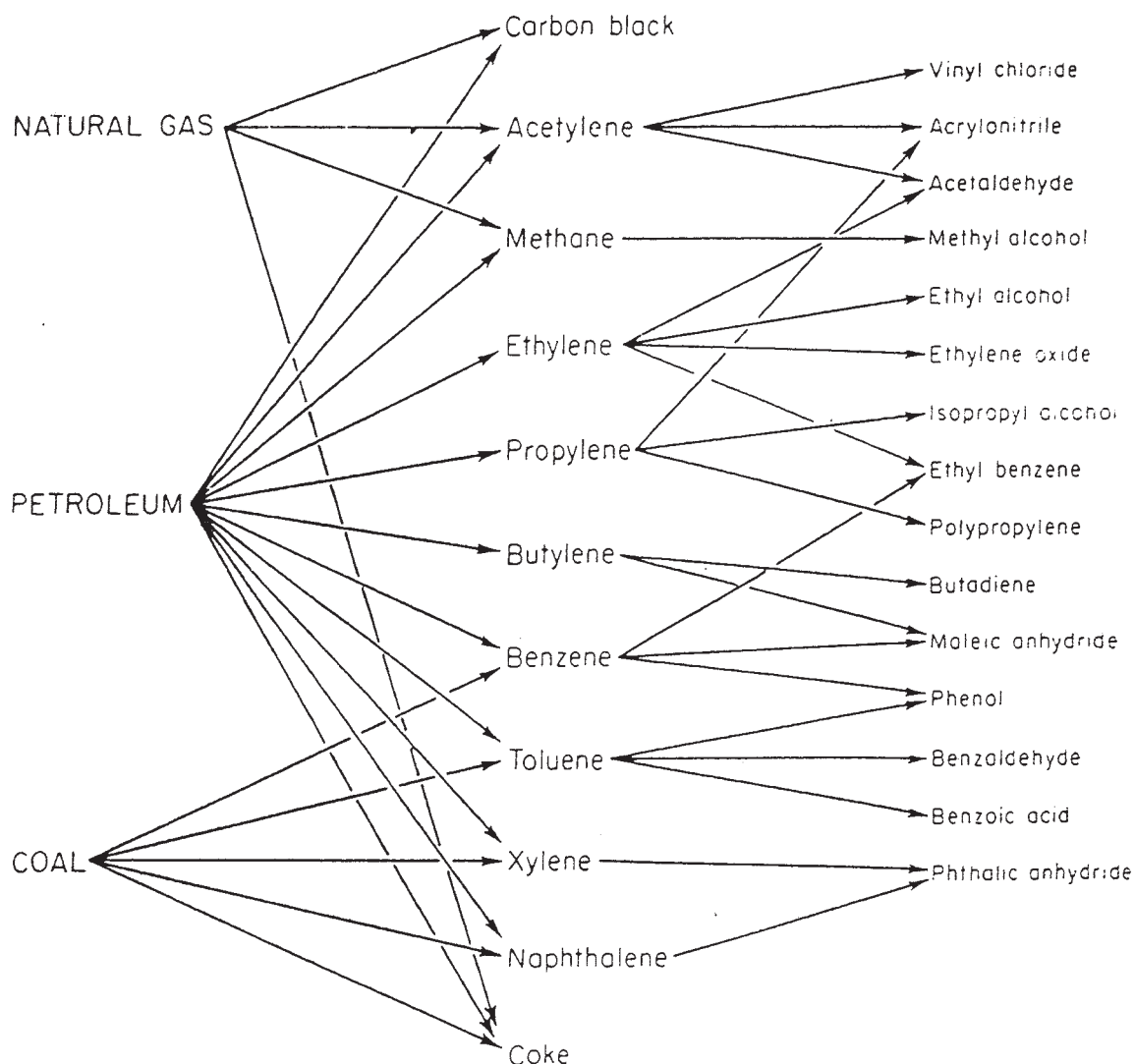


Fig. 37.6. Interrelationship of precursors from natural gas, petroleum cuts, and coal. (Marshall Sittig.)

3.13×10^7 kg/year. Dealkylation of a selected reformat stream using chromate-aluminum carbide catalyst with a 10-s exposure gives a product which is purified to be purer than that formed from coal tar. The Hydeal process by Ashland Oil Co. is one of the processes used.

LIGHT DISTILLATES. Aviation gasoline, (automobile) motor gasoline, naphthas, petroleum solvents, jet-fuel, and kerosene are the fractions generally regarded as light distillates. Any given refinery rarely makes all of them. Gasoline is the most important product, and around 45 percent of the crude processed now ends up as gasoline. When the compression ratio of a motor is relatively high, the fuel can detonate in the cylinder causing noise (knock), power loss, and ultimately engine damage. Branched chain and aromatic hydrocarbons greatly reduce the tendency of a fuel to cause knocking. *n*-Heptane knocks very readily; 2,2,4-trimethyl pentane (formerly known as iso-octane) is an extremely antiknock fuel. The *octane number*, a measure of the suitability of a fuel for high-compression engines, is the percentage of iso-octane which, when added to *n*-heptane, knocks in a special test engine to the same degree as the fuel being tested. Certain substances, such as tetraethyl lead (TEL) and tetramethyl lead (TML) can be added to gasoline in very small quantities to raise the octane number dramatically. Because of doubts concerning the safety of lead in the environment, these most useful additives are now restricted or limited. Cleaner burning is achieved by adding intake system detergents.