Petroleum Plastics

Crude petroleum pumped out of the ground contains thousands of different chemical compounds. These compounds include semisolid materials such as paraffin wax and asphalt, as well as gases dissolved in the heavier components under extreme pressure conditions deep beneath the earth. When the crude petroleum is brought to the surface and atmospheric pressure, these gases boil out to become "natural gas."

Over 3,000 different substances are prepared from crude petroleum. Refineries convert the crude into end products and intermediate products including natural gases, gasolines, solvents, kerosenes, asphalts, vaselines, medicinal oils, and petrochemicals.

Though petrochemicals account for only about 5% of the world's oil production, their importance in manufacturing is disproportionate. Petrochemicals are used to make adhesives, surface coatings, drugs, pesticides, and fertilizers. About half of the petrochemicals produced, however, are used to manufacture plastics, particularly polyethylene, polypropylene, polystyrene, and vinyl, and also synthetic fibers such as nylon, polyester, acrylic and acetate, and synthetic rubbers such as styrenebutadiene, butyl, nitrile and polychloroprene.

Originally, simple refining of crude oil was enough to separate natural gas and gasolines consisting of only a few hydrocarbons by distilling crude petroleum through fractionation columns. Early refining processes could separate methane, ethane, propane, butane, isobutane, and pentanes. More sophisticated fractionating columns could further isolate petroleum compounds with similar boiling points.

The petrochemical industry began primarily in the United States. Before 1920, the only petrochemical widely available was carbon black, which had been manufactured from natural gas since the 1870s. Interest in petrochemicals was stirred during World War I, when wartime activities caused shortages of many chemicals for civilian and military uses. Primary among these was toluene necessary for the manufacture of explosives, such as trinitrotoluene or TNT; several U.S. refineries altered their processes to emphasize production of toluene to the detriment of other petrochemicals.

Thermal "cracking" (conversion of heavy fractions to light fractions) of propane to produce ethylene also became commercially feasible in the early 1920s. Ethylene, along with butylene and propylene, became a primary petrochemical through the 1930s. The demand for ethylene and propylene grew so exorbitant that ambitious new cracking processes were developed to increase the proportion of these molecules. A single modern cracking plant can produce a billion pounds of ethylene a year.

E.W. Fawcett and R.O. Gibson at Imperial Chemical Industries in Great Britain developed high-pressure technology in 1934 that allowed them to be the first to polymerize ethylene. Commercial production of their "polyethylene" began in 1939. Plastics developed from ethylene established entirely new markets and displaced existing natural materials including wood and metals.

Ethylene is the hydrocarbon consumed in the largest volume when making other plastics such as polyvinyl chloride and polystyrene. It is also the raw material for acetate rayon fiber, cellophane, vinyl, and synthetic rubber.

In the 19th century, it had been discovered that monomers such as methyl methacrylate, styrene, and vinyl chloride could be polymerized. F.E. Matthews took out the first patents on the possible uses of styrene (also called vinylbenzene) in 1911. Monomeric styrene was present in coal-tar byproducts, but the processes necessary to remove styrene from this source proved too costly. When styrene became more widely available from petroleum refining, though, commercial production of polystyrene became possible in the late 1920s and 1930s.

Vinyl chloride, a gas at room temperature, is easily prepared from either ethylene or acetylene. Polymerization of vinyl chloride was studied extensively in 1916 by I. Ostromislensky, who attempted to dehalogenate the polymer into a rubberlike substance. This proved impractical, and it was not until the late 1930s that polyvinyl chloride (PVC) became a commercial success.

Practically infusible, PVC proved difficult to work with until a new technique of mixing the ingredients with polyvinyl acetate before polymerization yielded an easier-to-handle copolymer that would accept plasticizing materials to improve its flexibility. By varying the ratio of chloride to acetate, manufacturers could tailor the material's stiffness. PVC is used as a wire insulator, sheet stock, and synthetic rubber. Dry-spinning PVC produces filaments that can be woven into chemically resistant fabric.

Propylene is used to make polypropylene (Orlon) and polyacrilonitrile (Dynel). Propylene is also an intermediate in the manufacture of acrylic plastics such as Lucite or Plexiglas.

In 1935, nylon was discovered by a DuPont research team headed by Wallace H. Carothers. Originally intended to be used as fibers, some nylons are also made into plastic materials. The knowledge gained by Carothers and others about the synthesis of nylon led to the subsequent development of many other petroleum plastics. Nylon appeared commercially in 1939-1940, but was originally retained for exclusive military use.

By the end of the 1930s, petroleum refining took place on a large enough scale that supplies of hydrocarbon raw materials for producing plastics were virtually unlimited. By 1940, new petrochemicals and new chemical processes had become commercially successful. All this placed the United States in an advantageous position with the onset of World War II. Huge wartime demands for materials to replace rubber and metals provided the impetus for new production techniques and facilities.

Up to this time, the United States was virtually the only country developing a petrochemical industry; however, World War II left other European countries scrambling to catch up. Not until after the war were huge petroleum deposits uncovered in the Middle East and north Africa. The first large-scale petrochemical operations began in Great Britain after 1950; Italy, France, and West Germany soon followed.

After 1946, petroleum plastics, synthetic fibers, and synthetic rubber boomed in the commercial marketplace. New fibers were introduced to the public and caught on quickly. Polycarbonates appeared on the market in 1959; polysulfones appeared in 1965, and polyphenylene in 1966.

Production of petrochemicals during the 1960s accounted for more than half of the world's total organic chemical production and a third of total chemical production.

In and around an automobile engine alone are plastics, fuels, lubricants, antifreeze, filters, wire insulation, and gaskets—all based on petrochemicals. Now, petroleum-based plastics and other materials derived from petrochemicals are so prevalent in our daily lives as to seem indispensible.

Kevin J. Anderson

https://doi.org/10.1557/S0883769400040926 Published online by Cambridge University Press

FUTURE MRS MEETINGS

■ Fall Meetings ■

1992 November 30-December 4
Boston, Massachusetts

1993 November 29-December 3
Boston, Massachusetts

1994 November 28-December 2
Boston, Massachusetts

1995 November 27-December 1
Boston, Massachusetts

1996 December 2-6
Boston, Massachusetts

1997 December 1-5
Boston, Massachusetts

■ Spring Meetings ■

1992 April 27-May 1
San Francisco, California

1993 April 12-16
San Francisco, California

1994 April 11-15
San Francisco, California

1995 April 17-21
San Francisco, California

1996 April 22-26
San Francisco, California

1997 April 7-11
San Francisco, California

https://doi.org/10.1557/S0883769400040926 Published online by Cambridge University Press