Petroleum and Downstream Products

Oil products, from feedstocks to plastics, created the modern world.

MICHAEL J. FELTON

Petroleum has been the fuel for the dramatic changes that occurred during most of the 20th century. Ever since it began to be exploited, that dark liquid found so abundantly in certain regions of the world has been both a fuel and source of material product for the chemical industry. In both transportation and chemical product development, advances in petroleum processing were made for the same reason—the replacement of natural products.

Starting in 1854, George Bissell became fascinated with "rock oil" that was demonstrated at his alma mater, Dartmouth College. Bissell saw the commercial potential of this product to address the dependence on whale or coal oil for illuminating lamps. He organized a company and commissioned a Yale chemist to analyze the oil, which indicated that lubricants and waxes could also be produced. Other individuals primarily sold rock oil as a medicine, and some was sold as lamp oil. The company now had to obtain the oil, and Bissell hired Edwin Drake to drill a well to extract oil. Most other rock oils were either collected at the surface or were obtained from wells drilled for salt extraction. Drake struck oil on August 27, 1859, and combined with refining technology invented in Britain by James Young, the oil industry was officially started.

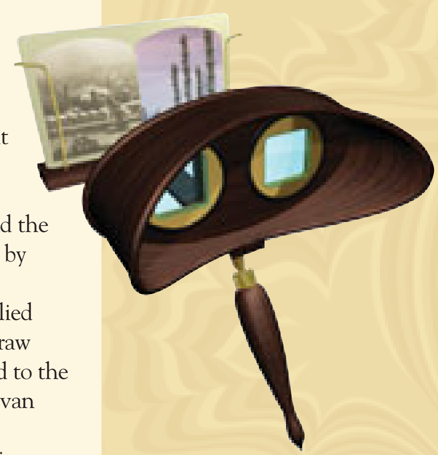
Many small oil companies started as commercial oil production spread, and by 1869, Cleveland, OH, was the oil capital of the world. There, in 1870, John D. Rockefeller formed the Standard Oil Company from several oil companies in which he was involved. Rockefeller's negotiation talent, along with his various partners' strengths, allowed Standard Oil to become so dominant that it inspired the Sherman Anti-Trust Act, which was used to divide the company in 1911. The various parts of Standard Oil are still well known today. For instance, ExxonMobil was formed from Standard Oil of New Jersey (Esso and Exxon) and Standard Oil of New York (Mobil) years after they were separated. Other Standard Oil progeny include ChevronTexaco (Chevron was formerly Standard Oil of California) and BP. BP purchased Standard Oil of Ohio and Atlantic Richfield (ARCO), formerly Atlantic Petroleum Storage Co., and merged with Amoco (Standard Oil of Indiana).

Standard Oil also exported its refined and crude oils, which led to industry development in other countries. In 1892, a British seashell importer's son commissioned a tanker ship to transport Russian kerosene to China and Singapore. This tanker was the first for a new company, called Shell, which ended up merging with its competitor, the Royal Dutch Company of the Netherlands, in 1907.

Using petroleum for lamp oil and lubricants left much of the crude oil unused. Fractions such as gasoline and naphtha were often dumped. However, they would later provide inexpensive fuel for two inventions that would change the world: the car and plastics.

Plastics and Synthetic Polymers

The first truly synthetic plastic, Bakelite, was made in 1907 by Leo Baekeland. He combined phenol and formaldehyde to produce a hard plastic—the first of what are known today as phenolic resins. The condensation reaction between phenol and formaldehyde produced a thermoset plastic that could be molded but could also be heated again and remolded. Unlike shellac, it would not burn, boil, melt easily, or dissolve in solvents, but its most important use was as an electrical insulator. In 1927, the patent on Bakelite expired, and the Bakelite Company was eventually acquired by Union Carbide.



Although natural rubber was being supplied from Asia and South America, the price of raw natural rubber was highly volatile, which led to the search for a replacement. In 1901, Russian Ivan Kondakov produced rubber by reacting dimethylbutadiene with potash. In 1909, Fritz Hofmann used a process similar to Kondakov's at

Top: Oil refinery, Photodisc

Center: Wallace Carothers in 1935, *Chemical & Engineering News*

Above: Polystyrene plant in China, *Chemical & Engineering News*

Germany's Bayer to produce polyisoprene, but it was not marketed because it proved to be too expensive. A year later, another Russian, Sergey V. Lebedev, made polybutadiene from ethyl alcohol.

Hofmann finally succeeded in 1912 in making an economic rubber. Polymethylisoprene, or "methyl rubber," was less expensive because it could be made from acetone. Rubber prices crashed the following year, halting production of methyl rubber, but Germany revamped its manufacture during World War I when both Bayer and BASF collaborated in its production.

I.G. Farben, ICI, DuPont, and the Soviet Union

In spite of Germany's defeat in World War I, ties between its chemical companies remained, and in 1925, a conglomerate was formed called Interessen-Gemeinschaft Farbenindustrie AG, better known as I.G. Farben, from companies such as Agfa, Casella, BASF, Bayer, Hoechst, Hüls, and Kalle. The British followed suit, merging Nobel Explosives, Brunner Mond, United Alkali, and British Dyestuff Corp. into Imperial Chemical Industries (ICI) in 1926. Although the United States did not merge its chemical companies into a conglomerate, it had DuPont—one of the few U.S. chemical companies expending significant resources on R&D. These three major companies, and the Soviet Union, made many of the advances in polymer chemistry between World War I and World War II.

The first challenge after World War I was the development of a better synthetic rubber. I.G. Farben began research into synthetic rubber in 1926, but the Soviet Union built the first pilot plant in 1930. The German and Soviet rubbers were similar, using sodium to form polybutadiene. I.G. Farben called its rubber "Buna" (butadiene and Na) and soon began producing Buna S and Buna N, which contained styrene and nitrile, respectively. Buna N was an economic success—even during the depression—because it was oil resistant, unlike most other natural and synthetic rubbers.

DuPont provided two major stepping-stones during the 1930s. First, in 1931, researchers at the DuPont Research Station in Delaware, led by Wallace Hume Carothers, synthesized neoprene. Second, Paul Flory—who in 1974 was awarded the Nobel Prize in Chemistry—created a mathematical theory of how polymerization and cross-linking occur. Carothers' group at DuPont went on to synthesize other forms of neoprene (polychlorobutadiene) and polyester, and in 1934 the group discovered nylon. Neoprene was eyed for rubber tire production but proved unsuccessful; however, it was one of the first polymers produced from petroleum sources.

In the late 1930s, ICI developed two new polymers, polyethylene and poly(methyl methacrylate). Although polyethylene could not be used to insulate high-voltage wires, it was an excellent insulator of high-frequency cables, such as those used in long-distance communications, and even radar. DuPont and ICI had a cross-licensing agreement allowing DuPont to develop and market these new polymers in the United States while ICI gained access to nylon and other DuPont polymers.

DuPont began commercial production, but not mass production, of neoprene in 1933. This and other polymer plants depended on feedstock from various sources, but most used coal tar or other coal by-products. Soviet synthetic rubber factories used an alcohol-based process, but in 1936, the Soviets built a petroleum-based polybutadiene plant, providing a glimpse of the future.

War and the Rise of Petrochemicals

The German government funded rubber research as well as coal liquefaction research during the 1930s in an aim to become self-sufficient. The United States was less prepared and accelerated its synthetic rubber plan after the Japanese cut off access to natural rubber from Asia.

The United States assigned cooperative work to key industries as part of the war effort. Research into synthetic rubber production was to be conducted jointly by the four major rubber manufacturers—Goodyear, B.F. Goodrich, the U.S. Rubber Company (Uniroyal), and Firestone—as well as the Standard Oil companies and several chemical companies. Before the war, Standard Oil of New Jersey (Exxon) had developed technologies to produce butadiene from petroleum instead of coal.

The Rubber Reserve Company determined that I.G. Farben's Buna S would be the material used for the bulk of rubber production, made possible by seized patents. Dow Chemical was placed in

GLOBALIZATION

Petroleum and petrochemicals have always been a global industry as demand and supply have shifted around the world. One region where demand is increasing very rapidly is Asia.

Japan has led the region in economic development, but as the economies of South Korea, Thailand, Malaysia, Singapore, Indonesia, and Taiwan have developed over the past 30 years, demand for petrochemicals has risen in kind.

The rapid increase in demand has many companies investing in increased capacity, with most of it located in China. Foreign companies investing in China are required to have local partners; BASF is building an ethylene cracker with Yangzi Petrochemical, BP has partnered with Sinopec, and Shell is working with CNOOC. Other companies are increasing production in order to export to China. Formosa Plastics Corp. (Taiwan), Mitsui Chemicals (Japan), and Nippon Petrochemicals (Japan) are all expanding propylene production for domestic and export demand.

With the increased demand in Asia and throughout the world, oil-rich regions such as the Persian Gulf will continue to supply the extra demand for crude oil, but they are also working on supplying higher-value products such as petrochemicals. For example, countries like Saudi Arabia are investing more resources into producing higher-value products than crude oil. The Saudi company SABIC (Saudi Basic Industries Corp.), started in 1976, has rapidly grown to become a major producer of petrochemicals. SABIC is now the third-largest ethylene producer in the world. Outside companies are also working with the state oil companies in this region. Japan's Sumitomo Chemical is working with Saudi Aramco (Saudi Arabia's state oil company) on a large refinery petrochemical project.

charge of styrene production, which also involved Monsanto, Union Carbide, and Koopers. The U.S. government provided about $700 million for the construction of plants.

Other plastics were also seen as essential to the war effort. Polyethylene from ICI became the secret that allowed the Allies to build lightweight radar systems that could be loaded onto a plane or ship. Plexiglas and Lexan (acrylics) provided plane canopies that were stronger and lighter than glass. Poly(vinyl chloride) (PVC) was finally perfected by Waldo Semon at B.F. Goodrich and used to make raincoats and bug nets, and in the form of Saran made by Dow Chemical, it protected planes during transport. Teflon was essential in the separation of uranium-235 from uranium-238 under extremely corrosive conditions for the Manhattan Project.

The oil industry was pushed to dramatically increase production to meet the demand for motor and aviation fuel as well as new petrochemicals needed for rubber (butadiene and styrene) and other polymers. The demand for aviation fuel and butadiene overlapped because butylene and butane were needed to make high-octane aircraft fuel.

The oil industry turned to technology it had developed in the 1920s and 1930s to meet the expanded demand. Catalytic cracking, alkylation, and catalytic reforming were all applied to increase usable products from a given amount of crude oil.

After the war, U.S. refining capacity increased 29%, and the products from refineries had become significantly more valuable. Benefiting from the fact that before the war the United States had 71% of the world's refining capacity, U.S. companies were clear leaders in oil refining and the new field of petrochemicals.

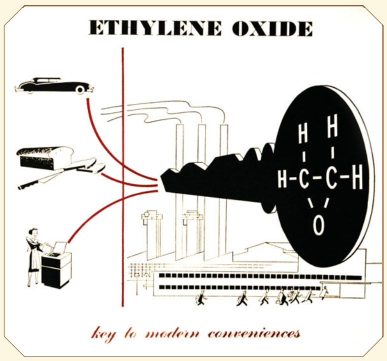
Commercial Explosion

After World War II, new uses for plastics and a dramatic increase in consumer demand for plastics created an extremely healthy petrochemical industry. In the early 1950s, Amoco, Phillips Petroleum, and DuPont began working on developing new polymers. In 1953, Karl Ziegler at the Max Planck Institute for Coal Research discovered that polyethylene could be made at much lower pressures using an organometallic catalyst than the very high pressures that ICI was using. The resulting polymer also had a higher density and higher melting point.

Polypropylene was discovered around the same time, but its central patents were bogged down in litigation. However, in 1957, Hercules began making polypropylene to use in bottles that could withstand the heat of pasteurization, leading to use in consumer products such as food containers. By 1961, there were at least nine North American producers of polypropylene, but the Italian company Montecatini sued Phillips Petroleum for patent infringement. Phillips Petroleum won patent protection in 1983. Since then, polyethylene and polypropylene have become the most widely used plastics in the petrochemical trade.

The Ethylene and Propylene Kings

Production of plastics reached more than 107 billion pounds in 2003 in North America, and although not final products, 51 billion pounds of ethylene and 35 billion pounds of propylene were produced, accounting for a large segment of the industry. Ethylene and propylene have become the predominate feedstocks because they can be used to produce a large array of plastics.



More than half of ethylene is used to make polyethylene for everything from pipes to milk jugs, but it can also be converted to ethylene oxide to produce detergents and to ethylene glycol for food packaging and textiles. Ethylene is also used to make styrene monomers, which can be polymerized to make polystyrenes like Styrofoam and styrene-butadiene rubber for automobile tires. Propylene is used to make polypropylene plastics and to make acrylonitrile for producing acrylic polymers, propylene oxide for polyurethanes, oxo alcohols (PVC plasticizers), cumene for epoxy resins and polycarbonate, and isopropyl alcohol.

In 2003, Dow was the largest producer of ethylene in the world. The chemical company first entered the plastics market in 1935, and in 2000, it acquired another key chemical company, Union Carbide. ExxonMobil comes in second, producing more than 16.6 million pounds of ethylene. In addition, many producers of ethylene and propylene manufacture some of their products as joint ventures with other companies, including many state oil companies. For instance, Dow operates joint ventures with Petrochemical Industries Company, the state oil company of Kuwait, and with NOVA Chemicals, a Canadian ethylene producer.

The volume and variety of manufactured polymers have increased dramatically since 1907, and the trend should continue for the foreseeable future. While production of feedstocks has matured, new polymers and new uses for existing polymers will continue to drive the industry. Human history is categorized by the materials used—the Stone Age, the Iron Age, the Bronze Age—are we in the Plastic Age? ◆

Center: Dow Chemical Co. ad, 1950, *Chemical & Engineering News*