

CATALYSIS CHRONICLES

Industrial process began as more art than science but ended up powering a planet and leading to new chemicals

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FRENCH MECHANICAL ENGINEER Eugène J. Houdry enjoyed racing cars, but during the early 1920s that was hard to do. At the time, France produced little petroleum or gasoline, and worldwide supplies were tight. Houdry's hobby eventually led him to develop what became one of the world's most industrially important processes—a catalytic method for converting, or “cracking,” crude oil into usable components for fuel.

Although Houdry's initial interest was personal, his work quickly had societal impact on a global scale. New catalytic methods for petroleum processing revolutionized the energy industry. Moreover, Houdry helped spark a “catalytic revolution” that made catalysts key tools within the broader chemical industry, according to a 1984 profile by then Ohio State University chemistry professor Charles G. Moseley (*J. Chem. Educ.*, DOI: 10.1021/edo61p655). Catalytic cracking enabled the production of high-quality fuels, which were critical during World War II and helped push open the door for oil to become more widely used as feedstock for most downstream chemicals.

Houdry began working in 1923 with pharmacist E. A. Prudhomme to explore a catalytic means to produce gasoline from coal, but he abandoned the process because it wasn't cost-effective. By 1927, Houdry had found that naturally occurring aluminosilicates could selectively convert the larger molecules in crude oil to shorter ones more usable for gasoline. Prior to this discovery, petroleum was distilled, largely to get kerosene for lighting, and later cracked thermally under heat and high pressure to make gasoline.

When Houdry began his work, industrial catalysis

was still more art than science, although industry operated catalytic processes to produce sulfuric acid, methyl alcohol, isopropyl alcohol, and some other chemicals. The conversion of atmospheric nitrogen to ammonia by the Haber-Bosch process, commercialized in 1910, was among the most important catalytic routes. The need for fertilizers and later for ex-

plodes during World War I drove its use.

In 1931, Houdry moved from France to the U.S. and set up the Houdry Process Corp., in partnership with Vacuum Oil Co., in New Jersey. The Great Depression slowed work, but eventually a catalytic cracking unit went into operation in 1936 at a Socony-Vacuum Oil site in Paulsboro, N.J. In 1937, the first full-scale commercial plant went onstream at Sun Oil's Marcus Hook refinery. The Pennsylvania site is now a National Historic Chemical Landmark.

Houdry's catalytic cracking produced twice as much gasoline from the same amount of crude oil as other available processes. It also yielded a higher-quality fuel with a larger percentage of high-octane components. High-octane fuels improve engine power, speed, and efficiency. Aviation fuels available at the time had an octane rating of about 70–80, and the most desirable high-compression airplane motors of the day—on the cusp of World War II—required 100-octane fuel.

“While there has been some controversy as to the extent of our crude oil reserves, there has been much more concern as to where sufficient supplies of aviation gasoline were to be secured,” reported C&EN's first incarnation, *Industrial & Engineering Chemistry News Edition*,

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RALLY 'ROUND
Aviation fuel produced through catalysts at Shell Oil was critical to World War II efforts.



in February 1939. “This anxiety has been heightened since the recommendation has been made that a 20-fold increase be made in the number of American fighting planes within the next few years.”

“Thanks to the new catalytic cracking, a plentiful supply of such aviation gasoline is now assured,” *IE&C* concluded about the new sources of 100-octane fuels. Although catalytic cracking came into play quickly, with 15 units in place by 1939, a major drawback was that coke deposits inactivated the catalyst. The batch process then had to be stopped so the catalyst could be regenerated. To prevent this problem, a consortium of academic and oil company scientists developed a groundbreaking continuous, fluidized-bed catalytic cracking (FCC) method.

With the first large-scale FCC refineries in place by 1942, high-quality fuel production increased dramatically. Catalytic cracking was soon producing 90% of aviation fuel made in the U.S., France, and Great Britain. With high-octane fuels,

Allied airplanes were able to outperform those of the Axis nations, a turn of events that helped win World War II. By the end of the war, gasoline needs would be three times the amount that industry originally estimated would be required.

Other innovations in catalysis both before and during World War II also helped increase high-octane gasoline supplies. Catalytic alkylation, isomerization, and polymerization approaches emerged to make blending components that improved gasoline. Both Shell Development Co. and Standard Oil of New Jersey, for example, found ways to dimerize normal and isobutylene and then hydrogenate the product to make isooctane.

Universal Oil Products used acid catalysts to combine gaseous olefins into liquid dimers and trimers. Other refiners

soon added such “cat poly” units to make gasoline components from recovered gases. Shell also adapted a UOP alkylation process to make cumene for blending. By 1944, Standard Oil of Indiana was putting five new plants into operation to isomerize light naphtha, pentane, and butane.

Meanwhile, Germany had long been using catalytic chemistry developed in the 1920s by Franz Fischer and Hans Tropsch to convert mixtures of carbon monoxide and hydrogen, or synthesis gas, to hydrocarbons. Syngas from coal was more readily available than petroleum in Europe, and Fischer-Tropsch chemistry became an important route to liquid fuels there, albeit not as efficient then as catalytic cracking.

During the war, as Japan took control of the natural rubber plantations in Southeast Asia, catalytic processes emerged for making synthetic styrene-butadiene rubber. Among these was a catalytic dehydrogenation method Houdry invented to convert butane gas, a by-product of petroleum processing, into butadiene. Ironically, Japan was so “rubber-rich” that it set up operations to convert rubber into oil, commented Robert Price Russell, president of Standard Oil Development Co., in 1947.

War and its end brought further changes. Within just a few years, “we had built a whole new industry to support this war machine,” says petrochemical industry consultant Peter H. Spitz. “Plants that had been making war materials were there to feed the pent-up desires of the entire population,” he says about the postwar economic boom and moves to use the output for new consumer products.

“It was an entirely new ball game, because we had petrochemicals available to make entirely new and different types of products,” he adds. Within a short time, plants were making chemical products that were barely known before the war but that we take for granted today. Along with synthetic rubber, these materials included synthetic polymers such as polyethylene, vinyl, and nylon.

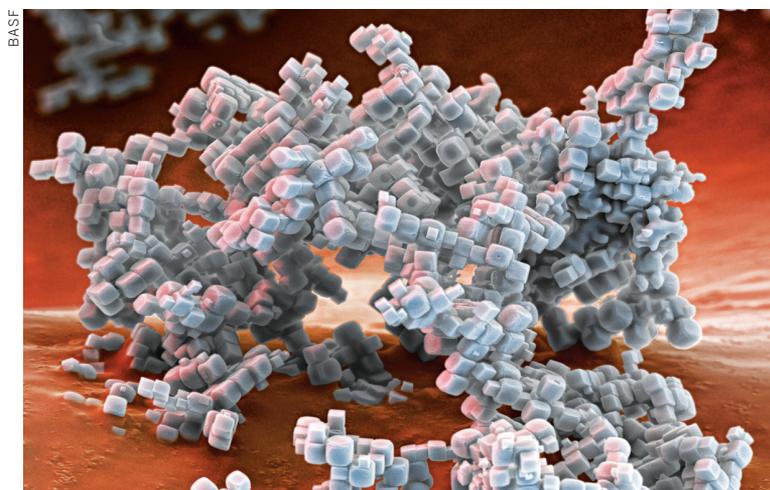
Catalysis helped the petrochemical industry expand as chemical derivatives were, to an increasing extent, based on hydrocarbon feedstocks coming from oil. Companies designed and built large, highly efficient chemical plants around new tech-

“Catalysis has changed its status from that of an art to a science.”

nologies, equipment, and processes, Spitz says. And these new plants were able to achieve economies of scale that had been unattainable in plants that used coal and cellulose as starting materials.

Petrochemicals soon went into making more downstream products, again using new catalyst-based production processes. In the 1950s, Ziegler-Natta polymerization catalysts were developed, and the polymer catalyst field continued to evolve for decades. Meanwhile, catalytic processes emerged in the mid-20th century for making chemicals such as acetic acid, acetaldehyde, terephthalic acid, and acrylonitrile. Acid-treated clays used for catalytic cracking were replaced by synthetic silica-alumina catalysts, and later by zeolite-based catalysts.

“Catalysis has changed its status from



NEW MATERIALS Crude aluminosilicate clays first used as catalysts have been transformed into structured specialty zeolites (magnification 8,000:1).

consume more than 99% of the catalysts now produced in this country, will be used up in a few hundred years, catalysis will still be of major importance.”

Catalyst sales today amount to about \$15 billion annually worldwide, and petroleum refining remains the largest end use. In 2011, refining consumed about

that of an art to a science only in the past 10 years,” said prominent Mellon Institute of Industrial Research (now Carnegie Mellon University) catalyst chemist Paul H. Emmett during his 1953 Pittsburgh Award address. “Even though fossil fuels, which

3.7 million metric tons of catalysts worth about \$5.6 billion, according to Freedonia Group, a Cleveland-based market research firm. Catalysts for chemical synthesis used another 458,000 metric tons, worth \$5.5 billion, and polymer production used

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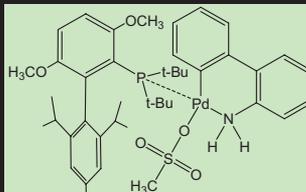
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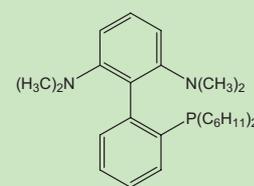
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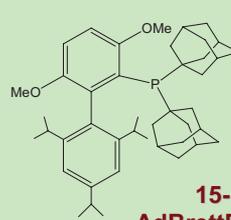
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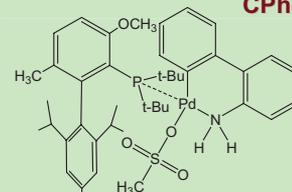
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just over 340,000 metric tons valued at \$3.6 billion. Catalysts are also widely used in controlling automobile and industrial emissions.

At least 90% of industrial chemicals are produced with the help of catalysts, according to John N. Armor, an industry consultant and former president of the North American Catalysis Society. Beyond petroleum processing and bulk chemical production, catalysts are critical in environmental applications such as controlling vehicle and industrial emissions—an area that Houdry himself entered after World War II—as well as for the synthesis of specialty and fine chemicals, including pharmaceuticals and agrochemicals.

Catalysts continue to drive new technologies and approaches to energy resource use, as people become less satisfied with using coal and petroleum, Armor says. “We look to catalysts for applications in fuel cells, photovoltaics, and biomass and natural gas conversion,” he says. “Energy is a much bigger topic around which catalysis can provide some resolution. And people will use catalysts because they present many opportunities that didn’t exist years ago.” ■



From C&EN Archives

Even 90 years ago, societal wants and needs were coming into conflict with natural resource availability. At the time, few realized that catalysis would enable more efficient petroleum processing to meet fuel needs and support the production of the vast majority of downstream chemical products known today. Columbia University professor Ralph H. McKee was quoted in C&EN’s first incarnation, *Industrial & Engineering Chemistry News Edition* (1923, 1(5), 2), saying that “petroleum production in the United States will begin to decline, probably within three years, and that it will be necessary to develop

the shale fields very soon, in order to insure a domestic supply of motor fuels.”

But by 1939, *I&EC* (1939, 17(3), 85) reported that the new catalytic cracking process, “together with the older ones, would make possible the production of gasoline for both automobiles and airplanes for the entire world from the crude reserves available in the U.S.”

In that same article, *I&EC* also noted that “it is estimated that the cost per mile of operating with the new gasoline will be in line with present motoring and flying costs, but a new era in automobile design will lie ahead because the superior characteristics of the new fuel will undoubtedly spur automobile engi-

neers to design and build far better engines.”

After the promise of petroleum was realized through catalytic methods, it would take several more years before chemical processes and a wealth of new products reached any scale. “All the organic chemicals including rubber and alcohol needed to meet the entire world’s needs for a year could be made from 10 days’ crude oil production. While negligible as a volume outlet for crude oil, the petroleum-chemical field is nonetheless of extreme importance,” said Robert Price Russell, president of Standard Oil Development Co., in a report on his Cadman Memorial Lecture (*C&EN*, 1947, 25(24), 1737).

Nobel Prizes Recognized Notable Developments In Catalysis

Between 1901 and 2012, the Nobel Foundation recognized achievements related to chemical and enzymatic catalysis at least 15 times, accounting for about 14% of the chemistry prizes and 19% of the prize winners. The prizes acknowledged an expanded scientific understanding, but many catalysis-related developments also had very practical uses.

Setting the stage, F. Wilhelm Ostwald received the Nobel Prize in 1909 for his work on catalysis and on the fundamental principles governing chemical equilibria and rates of reaction. Three years later, the prize went to Paul Sabatier for exploring the hydrogenation of organic compounds in the presence of finely disintegrated metals.

In 1918, the award went to Fritz Haber, who developed a process for the catalytic formation of ammonia from atmospheric nitrogen and hydrogen. Scaled up with the help of Carl Bosch, the Haber-Bosch process was one of the first major industrial routes to

basic inorganic chemicals.

In ensuing years, industrial catalysis expanded in the form of catalytic cracking, which enabled the efficient processing of petroleum into fuels and chemicals. Throughout the 1940s and 1950s, catalysts were invented to produce a range of downstream chemicals.

Plastics emerged as well, and Karl Ziegler and Giulio Natta were recognized in 1963 for discovering organometallic polymerization catalysts. Ernst Otto Fischer and Geoffrey Wilkinson independently studied the chemistry of organometallic sandwich compounds. This work, which helped de-

cipher how such compounds function as catalysts, garnered the 1973 prize.

In 1975, the Nobel Prize went to John Cornforth, who investigated enzymes, and Vladimir Prelog, who studied chemical reactions, for their work on stereochemistry. The fascination around chirality and catalysis continued in the work of William S. Knowles, Ryoji Noyori, and K. Barry Sharpless. The 2001 Nobel Prize rewarded their ability to control stereoselectivity via catalysis: Knowles and Noyori explored hydrogenation, while Sharpless looked at oxidation.

Over the past decade, these and other catalytic methods

have become critical tools in organic synthesis. In particular, they have expanded the potential of the field and the ability to efficiently produce specialty and fine chemicals, including many pharmaceuticals.

The subject of the 2005 Nobel Prize was a popular and useful molecular rearrangement known as metathesis. While Yves Chauvin helped to decipher the mechanism, Robert H. Grubbs and Richard R. Schrock made breakthroughs in discovering transition-metal catalysts to do the trick.

Similarly, the precise construction of complex organic molecules is possible through catalyst-driven carbon-carbon coupling reactions. Reactions using palladium-based catalysts bear the names of Richard F. Heck, Ei-ichi Negishi, and Akira Suzuki, who shared the Nobel Prize in 2010.