

A NATIONAL HISTORIC
CHEMICAL LANDMARK

THE FLUID BED REACTOR

BATON ROUGE, LOUISIANA
NOVEMBER 3, 1998



AMERICAN CHEMICAL SOCIETY
Division of the History of Chemistry and
The Office of Communications



PCLA #1 (Powdered Catalyst Louisiana), 1942.

This booklet commemorates the designation of The Fluid Reactor as a National Historic Chemical Landmark. The designation was conferred by the American Chemical Society, a not-for-profit scientific research and educational organization of more than 155,000 chemists and chemical engineers. Plaques marking the designation were presented to Exxon on November 3, 1998, for installation at the Baton Rouge Refinery and the Louisiana Arts and Science Center. The citation reads:

The first commercial circulating fluid bed reactor, PCLA #1 (Powdered Catalyst Louisiana), went on stream on May 25, 1942, in the Baton Rouge Refinery of the Standard Oil Company of New Jersey (now Exxon Corporation). This first use of powdered catalysts in continuous operation allowed the efficient cracking of heavy gas oils to meet the growing demand for high-octane fuels. PCLA #1 was dismantled in 1963 after 21 years of successful operation. Today, more than 350 fluid bed reactors, including PCLA #2 and PCLA #3, are in use worldwide for the manufacture of fuels, chemical intermediates, and plastics.

On the Cover: L to R: PCLA #1, #3, and #2, 1946.

Acknowledgments:

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FROM KEROSENE LAMPS TO AIRPLANES

The modern fuels manufacturing industry began in the mid-19th century with the separation of naturally occurring petroleum into three main fractions, naphtha, kerosene, and heavy oil, according to their boiling ranges. From the 1860s up to 1910, demand was primarily for kerosene for lamps. To make the lamps burn smoothly, it was important to separate all the low boiling naphtha fraction from the kerosene. Naphtha in the kerosene would make the lamp sputter, or, at worst, explode. Early fuels manufacturing technology was simply a physical separation by distillation, with no chemical changes in the petroleum fractions. The first chemical reactions were introduced to control odor and color. For example, sulfur compounds, which have very strong odors, were removed by reaction with strongly basic compounds. This chemical processing took place only on a very small portion of the product streams that went through the refineries.

Change in Demand

From 1910 to 1930 technological developments in other industries changed demands for various fuel products. Use of electric lighting caused slower growth in the market for kerosene, and the change in shipping from sail to steam and diesel engines (in ships and trains), plus the need for fuel to generate electricity, developed a market for the heavier, higher boiling fuel oils. However, the change that had the greatest impact on the fuels industry was the development of the gasoline engine and its application in both automobiles and airplanes. The demand for gasoline, which was made from the naphtha fraction, was much greater than the markets for other higher boiling liquid petroleum fractions.

Producing More and Better Gasoline

Engine builders had found that gasolines varied in their performance depending on the type of crude oil used for distillation. Better gasolines

allowed engines to run at higher speed with more power without damaging the engine. The poorer gasolines, in comparison, caused an engine to make a “pinging” or “knocking” noise and to run less smoothly. The “antiknock” quality of gasoline was expressed as an “octane” number on a numerical scale of pure chemical compounds as proposed in 1926 by Graham Edgar of the Ethyl Corporation. We now know that higher octane gasoline burns in a way that pushes the piston down smoothly during the power stroke. The lower octane gasoline burns too rapidly, and the sudden pressure rise makes the knock or ping in the engine cylinder, which can harm the engine.

In 1919, Charles F. Kettering and Thomas Midgley, Jr., of General Motors’ Dayton Engineering Laboratories Company, had begun work on controlling engine knock. In 1921 they reported that a mixture of tetraethyl lead and gasoline eliminated knocking and performed like a higher-octane gasoline. Upon development of efficient tetraethyl lead (TEL) synthesis methods a few years later, refiners could provide a constant octane gasoline product from a variety of naphthas. In the late 1960s, as gasoline consumption grew, careful analytical chemistry showed that the lead additives contributed to the spread of the heavy metal into the roadside environment. The Environmental Protection Agency of the U. S. government and the fuel manufacturers agreed to phase out the use of the lead additives. The technology used today to produce plentiful, high octane, unleaded gasoline started with technical innovations introduced in the 1920s and 30s.

Prior to 1925, the higher boiling heavy-oil molecules were chemically changed to smaller naphtha molecules by heating to decompose them using a process called thermal cracking. Between 1925 and 1935, Eugene Jules Houdry and his co-workers demonstrated that a catalytic cracking process provided a greater yield of gasoline. In addition, the cracked naphthas were higher in octane than only-distilled naphtha. The first full-scale commercial fixed-bed catalytic cracking unit began production in 1937. It changed the industry.

Installation of Conversion Reactors

The change to production of fuels by chemical conversion rather than distillation required that the refineries install expensive, large capacity chemical reactors. In addition, the Houdry Process Corporation was charging large licensing fees for the use of its technology. Oil companies not yet committed to install the Houdry process decided to explore other process methods that might overcome some of the known problems of the fixed bed reactors. This group of companies, called Catalytic Research Associates, included Standard Oil Company of New Jersey (now Exxon Corporation), M.W. Kellogg Company, Standard Oil Company (Indiana) (now Amoco Corporation), Anglo-Iranian Oil Company (now British Petroleum, Ltd., p.l.c.), Royal Dutch/Shell, Texaco, and Universal Oil Products (now UOP). The companies shared the results of process and catalyst testing they had conducted since the late 1920s. The large scale developments of this group were carried out at the Baton Rouge laboratories of Standard Oil Company of New Jersey.

Searching for a Solution

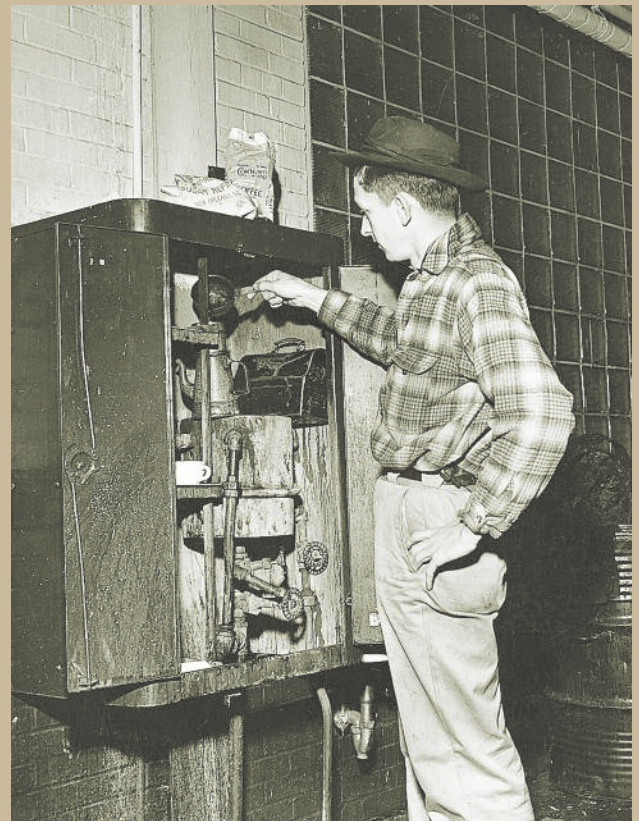
Typical catalysts in the early days of cracking were acid-treated clays or chemically made silica-alumina mixtures. Cracking catalysts that worked well exhibited the same behavior; they were active for a short period of time and then became covered with a deactivating layer called coke. This coke layer could be removed by heating and burning, but the regeneration was slow (minutes) compared to the time the catalyst was active (seconds). For every 20 molecules of heavy oil put into the cracking reaction, 18 would crack to smaller molecules, but two molecules would combine to make an even larger molecule. This larger molecule stuck to the catalyst surface and eventually became the coke that deactivated the catalyst. To this day, no exceptions to this behavior have been seen, although the amount of the heavy oil that becomes coke is less as catalysts have been improved.

The efficient way to use such catalysts, understood by all the organizations involved, was to move

the catalyst from one reactor (where cracking was done) to another reactor (where regeneration was done). The problem was to move the catalyst from the reactor, which contains the hydrocarbon feed and products, to the regenerator, into which air is forced to burn the carbon off the catalyst particles, without the regenerator air contacting the hydrocarbon. Steam was used as a stripping agent to separate the air and hydrocarbon vessels.

A Solution: The Fluidized Bed

The Catalytic Research Associates decided to focus on fine powder catalysts. In small units, it was easy to circulate the powders through a reactor, stripper and regenerator using screw-type conveyors, but these devices plugged up or wore rapidly in larger units. It was well known that a high-velocity gas flow blows powdered solids up (or down) a pipe,



A Baton Rouge refinery employee preparing coffee on a steam-heated coffee maker, 1946. Steam heat was used to adhere to the refinery's "no open-flame" safety policy. Similar coffee-making gadgets were installed throughout the refinery.

but Warren K. Lewis and Edwin R. Gilliland of the Massachusetts Institute of Technology, while working with Standard Oil Company of New Jersey, suggested that a low velocity gas flow through a powder might “lift” it enough to cause it to flow in a manner similar to a liquid.

This was quickly found to be true, and M. W. Kellogg Company constructed a large pilot plant in Standard’s Baton Rouge refinery. The pilot plant began operation in May of 1940. Based on its success, the construction of the first commercial plant began in September in the tense months just before World War II. The first Model I Fluid Catalytic Cracker (FCC) was completed on May 1, 1942 and began operating on May 25 in Baton Rouge at the Standard Oil Company refinery. Called PCLA-1 (Powdered Catalyst Louisiana), it was the first commercial fine powder circulating fluid bed reactor.

Between the May 1940 decision to build a Model-I design and the May 1941 decision to install additional catalytic crackers at the Baton Rouge refinery, large pilot plant work demonstrated that a Model II design used less steel and had a more efficient method of operation. The first two Model II units, PCLA-2 and PCLA-3 were built right next to PCLA-1.

Constructed in 1942 and 1943, they incorporated changes reflecting improved understanding of the process and the catalysts. They still operate today. PCLA-1 was shut down in October 1963 and subsequently dismantled.

Since the fluid bed designs needed less steel, less piping, and fewer valves than a fixed-bed unit for the same amount of heavy oil cracking capacity, war-time pressures to conserve strategic materials resulted in the construction of a total of 34 more FCC units. These reactors were built and operating by 1945 to help supply the large volume of high-octane aviation gasoline needed for the Allied forces in World War II, along with the feedstocks needed for the wartime synthetic rubber industry.

Contemporary Fluidized Bed Applications

After the war, demand for gasoline to fuel automobiles continued to increase. Today, more than 370 fluidized FCC units are in operation around the world. The FCC capacity in the US increased from 50 million gallons per day in 1950 to over 210 million gallons per day in 1992. Over the same time period, world capacity is over 460 million



PCLA #1, and #3 are shown in the 1946 photograph on the left. PCLA #1 was dismantled in 1963. The spot where it stood is to the left of the crane in the 1995 photograph (right) made during the replacement of PCLA #3’s regenerator.

PCLA #1 was a large unit by 1942 standards. It was 19 stories tall and built with 6,000 tons of steel, 3,500 cubic yards of concrete, 85 miles of pipe, and 63 electric motors. It had a catalyst inventory of about 100 tons and could process 588,000 gallons of fuel per day.

gallons per day, up from 63 million gallons per day. As the demands for gasoline volume and qualities have changed, the incorporation of new catalyst technology in these versatile fluidized catalyst units has enabled fuels manufacturers to provide cleaner burning gasolines.

Today many chemical reactors use fluidized beds. For example, the commercial synthesis of acrylonitrile, phthalic anhydride, aniline, maleic anhydride, and a portion of the polymerization of ethylene (to polyethylene) and propylene (to polypropylene) are all done in fluid bed reactors. There are noncatalytic processes, such as ore roasting, coking, combustion of coal and other solid fuels, as well as purely physical processes such as drying and conveying of fine particle products like flour, rice, and cement, which use the principles developed for the fine-particle fluidized bed.



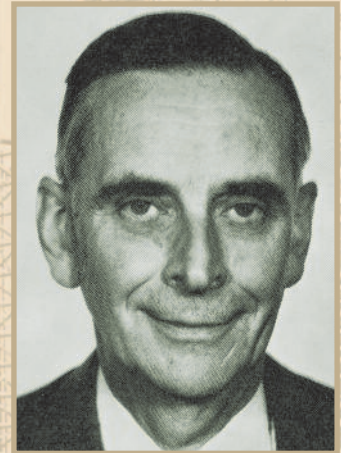
Eggar V. Murphree



Donald L. Campbell



Homer Z. Martin



Charles W. Tyson

The People Involved

The creation and development of the fluidized bed reactor system for catalytic cracking of petroleum was a cooperative effort that involved many talented scientists and engineers. The group, estimated at one thousand, represented the largest single concentration of scientific effort, up to that time, directed toward a common goal. Later during World War II, this effort was surpassed only by the radar and Manhattan projects in the United States.

Warren K. Lewis and Edwin R. Gilliland obtained patent coverage for the fluid bed idea. Professor Lewis was chairman of the Chemical Engineering Department at MIT and was one of the

best known chemical engineers in the country. The patent describing the circulating catalyst fluid bed reactor-regenerator named Donald L. Campbell, Homer Z. Martin, Eggar V. Murphree and Charles W. Tyson inventors, all employed by the Standard Oil Development Co. These patents were licensed to all the members of the Catalytic Research Associates.

FOR FURTHER READING

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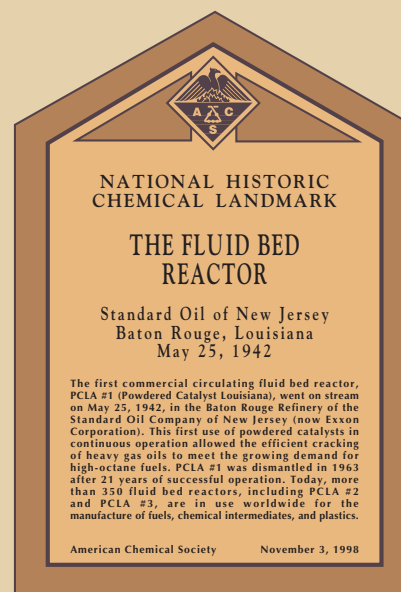
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THE NATIONAL HISTORIC CHEMICAL LANDMARKS PROGRAM OF THE AMERICAN CHEMICAL SOCIETY

The ACS National Historic Chemical Landmarks Program recognizes our scientific and technical heritage and encourages the preservation of historically important achievements and artifacts in chemistry, chemical engineering, and the chemical process industries. It provides an annotated roster to remind chemists, chemical engineers, students, educators, historians, and travelers of an inspiring heritage that illuminates where we have been and where we might go when traveling the diverse paths to discovery.

An ACS historic chemical landmark represents a distinctive step in the evolution of the chemical sciences and technologies. Designations of sites and artifacts note events or developments of clear historical importance to chemists and chemical engineers. Collections mark the contributions of a number of objects with special significance to the historical development of chemistry and chemical engineering.

This program began in 1992, when the Division of the History of Chemistry of the ACS formed an international Advisory Committee. The committee, composed of chemists, chemical engineers, and historians of science and technology, works with the ACS Office of Communications and is assisted by the Chemical Heritage Foundation. Together, these organizations provide a public service by examining, noting, recording, and acknowledging particularly significant achievements in chemistry and chemical engineering. For further information, please contact the ACS Office of Communications, 1155 Sixteenth Street, N.W., Washington, DC 20036; 800-ACS-5558, ext. 6274.



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American Chemical Society
1155 Sixteenth Street, N.W.
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