ALMER McDUFFIE McAFEE (1886 – 1972): COMMERCIAL CATALYTIC CRACKING PIONEER

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Many modern day authors identify the transition from the thermal to catalytic cracking of petroleum as the commercialization of the Houdry process patents (1) in the late 1930s and early years of the World War II. In actuality, commercial catalytic cracking of petroleum began with the anhydrous aluminum chloride-based "McAfee Process" in the years following the World War I. The process was developed and commercialized by the Gulf Refining Co. and is named after its inventor, Almer McDuffie McAfee.

Almer McAfee was a product of his times and the company he kept. No Eugene Houdry, he embodies the image of many industrial chemists of the time when chemical engineering was developing into a separate area of study. It was Almer McAfee and his contemporaries who solved the practical dilemmas of creating national vertically integrated petroleum companies following the dissolution of the Standard Oil Trust.

Early Years

Almer McDuffie McAfee was born near Corsicana, Texas on Sept. 24, 1886, one of eleven children of a local storekeeper. In June of 1894, when he was eight years old, city workers discovered oil while drilling community water wells (2). The Corsicana field became the first oil field of importance in Texas. On Christmas day 1898. the stills were fired on a Standard Oil Company financed 2000 barrel per day refinery at a site one mile from the oil field. It is not surprising that a youngster growing up during those boom days would develop a more than passing interest in petroleum technology.

McAfee attended the University of Texas where he earned the A.B. degree in Chemistry in 1908. In 1907, while taking a course in organic chemistry, he wrote next to the discussion of the Friedel-Crafts reaction in his textbook the words "Exceedingly useful" (3). This sentiment, expressed by his professor, Dr. J.R. Bailey, would sow a seed for his subsequent career.

Following receipt of his A.B. degree, McAfee spent two years as a graduate student and Tutor in chemistry at the University of Texas. In the Fall of 1910, he became a Goldschmidt Fellow in Chemistry at Columbia University. The next year, McAfee earned the Ph.D. degree in Chemistry, with major work in physical chemistry under the direction of J. Livingston R. Morgan. His 23-page dissertation was entitled "The Drop Weight of the Associated Liquids—Water, Ethyl Alcohol, Methyl Alcohol and Acetic Acid."

While attending Columbia, McAfee would continue a courtship with Marguerite Calfee, whom he had met while at the University of Texas, and who was working toward her Masters degree at Bryn Mawr at that time. In 1914, the two would marry in their home state of Texas where they would raise their three children. Their first child, the late Jerry McAfee, became a chemical engineer and joined Gulf Oil Corp. in 1945. He would rise through the ranks to become Chairman of the Board of Gulf Oil Corp. before retiring in 1981.

The Gasoline Problem

The Corsicana refinery of McAfee's youth was typical of refineries of the day. Petroleum technology was in its straight-run phase, in which the "natural" kerosine, gasoline, fuel oil, etc., fractions of the crude were collected by distillation and refined. The refining process involved treatment, typically with sulfuric acid, to remove color and objectionable odors.

At the turn of the century, gasoline fractions produced at the Corsicana refinery were collected and discarded into the local streams during the spring floods as they were of little value. This situation would not last long. Mass production of the automobile greatly increased gasoline demand throughout the first quarter of the century. In 1907, The Texas Company (now Texaco) became the first refiner to sell more gasoline than kerosine (4). By 1911, nationwide demand for gasoline exceeded the nation's kerosine demand. The gasoline demand was reflected in prices at the pump. During the years 1910 to 1913 gasoline prices increased from approximately 10 cents to 30 cents per gallon (1).

With petroleum technology still in its straight-run phase, the challenge to refiners was to find ways to obtain increasing quantities of gasoline from the crude. Many larger refiners hired industrial chemists specifically to develop methods to wring more gasoline from their crude stocks.

The Texas Company

It was in this climate that McAfee accepted a position at The Texas Company's Bayonne, New Jersey facility after receiving his Ph.D. in 1911. Initially employed in the testing laboratories, McAfee was unhappy with the nature of the work, desiring to become more involved in the challenging gasoline problem research and manufacturing end of the business. McAfee's supervisors agreed to send him to Texas in the fall of 1912 to become one of the first research chemists on staff at the company's Port Arthur facility.

The major part of The Texas Company's refining capacity was in Port Arthur. Located near the mouth of the Sabine River on the Gulf of Mexico, Port Arthur was a two-company town where both The Texas Company and Gulf Refining had built their first refineries in the early part of the century. The two companies were the offspring of the nearby Spindletop Oil Field discovery of 1901 (4).

A. M. McAfee, courtesy Mrs. Jerry McAfee

As a research chemist at The Texas Company, McAfee was supervised by George William Gray, who already had a long history in the petroleum industry (5). He had followed William Meriam Burton (Burton Process) as superintendent at Standard Oil's Whiting (Indiana) refinery in 1898. Gray, like Burton, was a Ph.D. chemist trained at Johns Hopkins. Gray left Standard Oil shortly after another Hopkins-trained chemist, Robert E. Humphreys, arrived in Whiting in 1900. He then went to the Sunflower Oil Co. and subsequently to The Texas Co. By 1912, he was employed in the Houston headquarters as the Chairman of the Refining Committee. As Chairman, he had direct supervision of the chemical research department and laboratory.

On his way to Port Arthur McAfee stopped in Houston, where he had a lengthy conversation with Gray. Much of their discussion centered on the gasoline problem and both old and new ideas about petroleum refining and cracking. One recent development in the field of industrial chemistry which interested several refiners was the work of David T. Day, who in 1906, had patented a process for the hydrogenation of unsaturated materials with nickel as a catalyst (6). It was known that unsaturates in the gasoline fractions imparted color and objectionable odors to gasoline, and it was hoped that catalytic hydrogenation processes would yield a "sweet" product. Gray's immediate interest was in refining (sweetening) distilled products by a hydrogenation process.

McAfee went to Port Arthur and initiated the work on hydrogenation research in early November, 1912. Although there was later some contention as to the specifics (7), Gray had instructed McAfee to distill the natural gasoline from the crude with the suggested addition of condensers located in a position to provide careful control of the boiling range of the collected gasoline fraction. This fraction was then to be hydrogenated, with the goal of sweetening the product. Several re-

agents were proposed as hydrogenation catalysts, including aluminum chloride.

After arriving in Port Arthur, in addition to his assigned duties, McAfee looked into other processes which included placing catalysts into the crude during the initial distillation process. One of the catalysts he utilized was anhydrous aluminum chloride. He discovered that, by applying the careful collection of the gasoline fraction via the double condenser system suggested by Gray, and with anhydrous aluminum chloride in the straight run still, he was able to obtain improved gasoline fraction yields which were water-white and odorless.

In December, 1912, he reported his initial success to his superiors in Houston. In January, Gray filed two patent applications based on the process developed by McAfee, without including McAfee's name. McAfee complained to Gray and ultimately to Gray's superior, Robert Holmes (Holmes-Manley Process). Not finding satisfaction, he ultimately sought a position at Port Arthur's other oil company, the Gulf Refining Co., taking his claim of priority in aluminum chloride cracking with him.

Table I
Precedent in Aluminum Chloride-based Catalytic Cracking and Polymerization.

Patents (Pre 1912)		
1877	Britain	C.D. Abel (for Friedel, C. and Crafts, J.M.)
1903	Britain	Adiassewitch
Literature (Pre 1912)		
1881	G. Gustavson	Kerosine to gaseous hydrocarbons
1888	C. Engler	Distilled fish oil to high boiling oils
1889	C. Engler	Distilled fish oil to high boiling oils
1893	C. Engler	Distilled fish oil to high boiling oils
1896	F. Heusler	Lignite tar distillates to high boiling oils
1902	O. Aschan	Olefin polymerization
1910	C. Engler	Amylene to Lubricating Oil

Gulf Refining Company

When McAfee presented himself to Gulf Refining, he found a supporter in George H. Taber, the general manager at Gulf's Port Arthur facility. Taber arranged to hire McAfee, promising to support the development of the aluminum chloride process, with McAfee as project leader. Gulf also supported McAfee's application for patents in competition with the Gray patent. This support would initiate a series of patent infringement claims, hearings, litigations, and appeals, beginning in 1913 which would not be resolved until 1928 (9). At that time the U.S. 5th District Court finally ruled that, although The Texas Company had a shop right (8) to the McAfee Process, the patented work was a creation of McAfee's and not Gray's. Although The Texas Co. funded research into its own aluminum chloride processes, no commercial cracking facilities were ever built.

After the issuance of the first McAfee Process patent in February, 1915, Taber publicly pronounced the McAfee Process to be a "commercial, scientific, and laboratory success (7)". Taber stated that the process "really is the proposition, more especially as the products it turns out are stable and are what the trade calls 'sweet'".

The first commercial anhydrous aluminum chloride cracking units were constructed at the Gulf Refining facility in Port Arthur in 1915 and went into operation in 1916. A second cracking still was built in 1918. By the 1920s Gulf had built a total of twenty seven stills at Port Arthur and three at their Fort Worth facility.

Precedent to Aluminum Chloride Catalytic Cracking

In his 1917 review, entitled "The Pyrogenesis of Hydrocarbons," E.L. Lomax expressed some surprise that either the Gray or McAfee aluminum chloride catalytic cracking patents were awarded in view of the precedent in patents and literature reports (9). He noted that aluminum chloride catalysis had a long history in and out of the petroleum industry, citing Elbs' "Synthetische Darstellungsmethoden," Volume 2, published in 1891 which devoted 45 pages to aluminum chloride. Also noted was Mayer and Jacobsen's 1902 edition of their book listing 178 references to various applications of aluminum chloride in synthetic organic chemistry. The

largely unrealized commercial promise of anhydrous aluminum chloride was summed up by Almer McAfee when he quoted von Baeyer's late 19th-century observation that the myriad uses of aluminum chloride sounded like a fairy tale (10).

The global literature contained several examples of both cracking and polymerization catalyzed by aluminum chloride (Table I). Most importantly, on December 5, 1877, C.D. Abel received a patent in England on behalf of Friedel and Crafts (11). This patent deals with the treatment of low-grade petroleum with 5 to 20 % anhydrous aluminum chloride, or a mixture of aluminum chloride and metallic oxides at 100° to 600° C. The oil was converted to light oils, gas, and heavy paraffin oils. The process was designed to produce lubricating oils, etc., from heavy hydrocarbons.

Given the precedent for aluminum chloride cracking, it is not surprising that other refiners of the day would also investigate this form of catalytic cracking. In his 1918 Willard Gibbs Medal Awardee Address (12), William Burton noted that the first two of the three years of the research that would lead to the development of the Burton Thermal Cracking Process (13) were occupied with attempts to develop an aluminum chloride-based cracking process. The efforts were abandoned because of the unavailability of a low-cost source of aluminum chloride and an inability to develop a method to recycle the catalyst. The development of a low-cost source of aluminum chloride by McAfee was the key feature which allowed Gulf to capitalize effectively on its patents.

Several other refiners also attempted to develop aluminum chloride catalytic cracking methods and/or to solve the catalyst availability and recycle problems (Table II). Of these, published reports indicate that only The Hoover Company ever attempted to commercialize their patents (14). They operated a plant based on their own patent, in Fairmont, Oklahoma in the early 1920s.

The McAfee Process was developed at the same time as Indiana Standard was licensing its Burton Thermal Cracking Process nationally. Gulf Refining chose to go against the industry trend and not license the Burton or other thermal processes in favor of the development of the McAfee Process and, later, its own thermal processes (15).

There were several advantages to the McAfee Process over its thermal counterparts (16). From the engineering standpoint the McAfee Process requires substantially lower temperatures and could be operated at atmospheric pressure. Thermal cracking processes employed minimum pressures of 60 - 100 psi. Coke deposits reacted with the steel used at that time, causing brittleness in the inner wall of the vessel. Vessels could, and did breach, causing fires and explosions.

Aside from the operational advantages, the quality of the product from aluminum chloride cracking had superior color and odor properties and better anti-knock performance than typical gasoline of the time. The octane scale had not been invented at that time, so Gulf marketed its improved performance product as Gulf No-Nox™ gasoline. Later studies showed that anhydrous aluminum chloride- cracked gasoline had an octane rating of 80 (17).

Table II
U.S. Corporate Anhydrous Aluminum Chloride Patent Initiators

Cracking Process Patent Initiators (1913-1925)
- 1913 - The Texas Co.
- 1913 - Gulf Refining Co.
- 1914 The Chemical Foundation
- 1919 - Standard Oil Co. of New Jersey
- 1922 - Universal Oil Products
- 1922 The Hoover Co.
- 1924 The Nitrogen Corp.

Synthesis or Recycle Patents (1914-1925)
- 1914 - Gulf Refining Co.
- 1916 - Alchlor Chemical Co./Standard Oil Co. NJ
- 1919 - The Texas Co.
- 1925 - Sinclair Refining Co.

As ultimately commercialized, McAfee's process utilized a batch operation in which 1000-bbl stills were charged with crude oil, which was heated to remove moisture and then treated with 1 to 5 percent anhydrous aluminum chloride. The stills were heated at 250 - 280° for 24 - 48 hours at atmospheric pressure. Air condensers were used to separate the high-boiling and low-boiling fractions, with the high boilers returned to the vessel. With proper control of the temperature of the vapor leaving the vessel and entering the final condenser, and sufficient time for reaction, McAfee found that high-boiling material could be converted to low-boiling oils. Pot residues were used for the paraffin and lubrication oil markets.

Industrial Synthesis of Aluminum Chloride

As noted previously, the major impediment to the widespread application of aluminum chloride cracking was the high cost of the catalyst. McAfee had paid $1.50 per pound and waited six weeks for delivery of the anhydrous aluminum chloride used in development of the refining process in 1913 (18). It took approximately one to one and a half pounds of catalyst to produce a gallon of gasoline. With pump prices at 30 cents per gallon the economics were not in Gulf's favor.

McAfee and Gulf realized that they were just embellishing von Baeyer's fairy-tale uses of aluminum chloride unless an economically feasible method of manufacture could be developed. It took three years and an investment of $1,000,000 by Gulf Refining to develop a practical, large-scale aluminum chloride synthesis (16). Because of McAfee's aluminum chloride synthesis work, Gulf Refining became not only a major producer, but by far the nation's largest producer of anhydrous aluminum chloride (Table III) (19).

The initial attempts by McAfee and Gulf to make aluminum chloride on an industrial scale, begun in 1915, involved the addition of chlorine to aluminum metal in fire clay retorts (16). The caustic nature of the chlorine gas quickly destroyed the retorts. They changed to fire brick retorts six months later, only to discover that chlorine at 1600° F also attacks brick, as it does porcelain which was subsequently tried, on the advice of ceramics experts. After two years of effort, success came in the form of briquettes of coal and bauxite charged into a chlorinating furnace consisting of two courses of fire brick behind a layer of powdered bauxite encased in an iron jacket. The largest furnace produced 40,000 lb. per day. The fire brick had to be replaced approximately every 100 days.

Table III:
U.S. Production of Aluminum Chloride
(Thousand Lb.) (17)

Year	Total	Anhyd.	Gulf	Gulf Percent(anhyd.)
1918-23			6,200	
1924	12,020		10,719	89
1925	26,665		21,387	80
1926	34,500		27,264	79
1927	35,260	29,200	26,550	75 (91)
1928	34,540	28,990	27,017	78 (93)
1929	34,102	28,574	26,840	79 (94)

The aluminum chloride produced was collected by sublimation. The product was only about 95.1% pure, with traces of iron trichloride, titanium tetrachloride, and other impurities. Nevertheless, the material was usable for petroleum cracking and for the dye or other synthesis industries. In the early days the aluminum chloride was sublimed into condensers of brick, which were cleared by hand. The brick condensers were 30 feet long, 12 feet high, and 6 feet wide. They would frequently become blocked and filled with carbon monoxide causing more than a few explosions and shattering of the condensers. Later, the aluminum chloride was condensed into a 16-inch vertical iron pipe with revolving vertical scrappers. Gulf ultimately found in Suriname a source of cheap high grade bauxite. In 1925, Gulf opened the largest electrolytic chlorine and caustic plant in the US at Port Arthur for the purpose of serving their anhydrous aluminum chloride-based cracking and refining operations (20).

Cracking Yields to Refining and Lubricating Oil Production

Even as the McAfee Cracking Process was being developed and commercialized, refiners, including Gulf, were taking advantage of new engineering materials and new ideas in thermal cracking. By the late 1920s engineering improvements had overcome much of the difficulty in high-temperature and high-pressure operation. These improvements in thermal cracking processes reduced the cost of gasoline production by the competing thermal process methods of the day (21). Balanced against the cost of the catalyst, the McAfee cracking process was no longer economically competitive. The introduction of tetraethyl lead as an anti-knock agent offset the process other major advantage of superior anti-knock properties. In 1929, approximately one year after prevailing in the patent battle with The Texas Co., Gulf terminated McAfee cracking operations.

The McAfee Process research demonstrated the ability of anhydrous aluminum chloride not only to crack but also to rearrange or polymerize petroleum hydrocarbons (4). Temperature was discovered to be the key factor in selection of the desired properties of the aluminum chloride-petroleum interaction. This knowledge led McAfee's team to develop an anhydrous aluminum chloride refining process requiring much smaller amounts of catalyst to improve octane rating and also

to produce a premium grade of lubricating oil. Anhydrous aluminum chloride is still utilized in the petroleum refining under the generic name of "Alchlor process refining." In 1927 Gulf began aluminum chloride-based production of high grade oil under the Gulfpride™ name. They continued to produce the oil via the McAfee Process until the late 1960s

With the lower demand for aluminum chloride in the lubricating oil refining process, Gulf was faced with a large investment in catalyst production capacity of 75,000 lb. per day. Gulf met this challenge by having McAfee announce at the 1929 national meeting of the American Institute of Chemical Engineers that Gulf would make aluminum chloride available in carload lots at 5 cents per pound (13). With production costs of 3 cents per pound as early as 1923, Gulf would be able to profit in a market where bulk prices were 12 cents per pound before McAfee's announcement.

The industrial community met McAfee's announcement with revelry. It meant that the fairy-tale uses of aluminum chloride could become reality in the industrial setting. An editorial in *Industrial and Engineering Chemistry* in August, 1929, highlighted the new availability of aluminum chloride(22):

> In many a laboratory the long list of Friedel and Crafts syntheses, worked out and described some fifty years ago, will now be reinvestigated from the standpoint of commercial utility, since at last aluminum chloride is available in carload lots.

Of the McAfee team at Gulf it was stated:

> Those who make fundamental reagents available to industry at a cost permitting more extensive use perform services the beneficial effects of which will be felt for many a year to come.

Despite calls to move to Gulf's research facilities in Pittsburgh, McAfee remained as Superintendent of the Aluminum Chloride Department in Port Arthur throughout his 38-year career with the company. At the time of his retirement on January, 1, 1952, he held 40 US patents, most on the manufacture and use of aluminum chloride in cracking and refining of petroleum. While the records of this period are missing, several former long-time Gulf employees have indicated that they could not recall any sales of aluminum chloride from the Port Arthur facility. As Gulf developed and brought on-line alternate production processes for high-grade lubricating oils in the late 1940s, the often troublesome production of aluminum chloride was abandoned.

McAfee had a reputation for ingenuity which was not limited to his career. In the early 1920s, he built a home in the Griffing park suburb of Port Arthur. To provide additional climate control, he installed pipes between the inner and outer walls of the house perimeter. Through these he circulated ground water from a shallow well on the property. This gave him additional cooling in summer and heating in winter.

McAfee was also prominent in civic affairs. He was a member of the Port Arthur Independent School District board of trustees from 1931 to 1941, serving as the board's president from 1934 to 1941. During World War II he was chairman of the Rationing Board of Southern Jefferson County, TX. He also served on the board of the Lamar Junior College (now Lamar University), where he was instrumental in expansion of the institution to a public, four-year college. McAfee became the first Chairman of the school's Board of Regents, serving one term. He was also active in the Port Arthur Chamber of Commerce and served on the national council of the Boy Scouts of America. He was an active layman in the Methodist Church in Port Arthur and was active in the Rotary Club. Following his retirement in 1952, McAfee remained active in civic affairs and operated a small farm in Woodville, TX. He passed away on October 12, 1972, at the age of 86.

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