CHAPTER 8
THE AUTOMOBILE – HOW PETROLEUM REFINING WAS DRIVEN

Until shortly after the Civil War it appears that half or more of the crude oil processed in primitive refineries was discarded. The only marketable products were kerosene for lighting, harness oil for preservatives, lubricants for the steam engine, and some gas oil for making town gas and for boiler fuel. Until the steam engine was in routine use, there was little demand for petroleum fuels at all. The emergence of the internal combustion engine and its application to the automobile created a need for a liquid fuel. Scientific data were developed where none existed, and engineering principles were created from art and observation. Chemical engineering literally 'fueled' this revolution of individual mobility. The modern age of petroleum refining was born out of this market demand—and that pattern continues to dominate - market demand pulled the development of refining capacity and technology.

This chapter is devoted to the interaction of the development of the automobile and its fuel. During most of this period the two industries leapfrogged each other on gasoline quality issues. Auto manufacturers and owners wanted better performance, and higher quality gasoline generated higher profits for refiners. The customers were quite willing to pay for improved performance. The history of this symbiotic relationship is described in four periods:

The First Hundred Years, 1840 to 1940

For much of this early era, the primitive refinery operation was focused on meeting a higher required flash point of kerosene, which was the major product and used almost exclusively for lighting. Building and home fire hazards were extreme, and there was little, if any market for the lighter fractions. Materials both lighter and heavier than kerosene were mostly discarded into rivers and lakes or burned.

The Automobile Industry Is Born.

There were a few steam-powered automobiles in the late 1800s, using a variety of solid and kerosene type fuels as an external heat source for the boiler. Essentially all the automobiles were in major cities. Their cost was so high that only the very wealthiest could afford one. There was no distribution system for fuels or parts and liquid fuels were very scarce and costly. By the turn of the century, quiet and reliable electric automobiles were displacing these clumsy and dangerous devices.

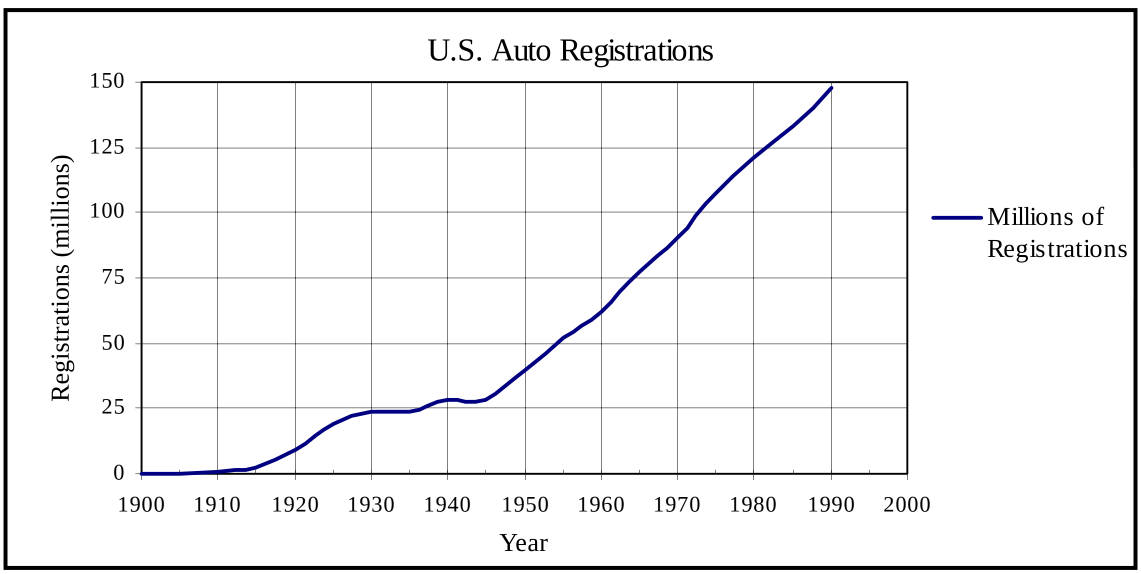
However, there was the slow and painful birth of an entirely new technology that would forever change the world - the internal combustion engine. Writing in an 1820 paper, a Rev. Mr. Cecil described an engine driven by explosions of hydrogen and air. In 1838, William Barnett, also of England, patented a gas engine that included compression of the fuel/air mix. Lenoir in France and Otto in Germany developed successful engines in the 1860s that were fueled with gas. The gasoline engine of today employs what is called the Otto cycle (4 stroke). These early engines were far from commercially feasible, lacking practical fuel and ignition systems, etc.

The internal combustion engine using gasoline as fuel was developed in 1885 by two names revered in the automobile industry -- Daimler and Benz. Working independently, they developed internal combustion engines that could power a cart or bicycle. In France in 1890, Lavassor and Panard developed the automobile as we know it using a Daimler engine. The following year they moved the engine to the front, which was considered a major improvement because it was no longer necessary to sit above it.

Open chain drives had the nasty characteristic of flinging grease onto clothes of the occupants, which severely limited the potential mass application. Then Renault replaced the exposed chain drive with the drive shaft and differential system. Mercedes-Benz later developed an enclosed chain drive with an oil bath and used it for many years because it was much quieter, more reliable, and able to transmit much more power than early gears, which suffered from crude manufacturing technology and poor lubricants.

In 1893, the Duryea brothers built the first auto in the United States. Several other carriage makers in the United States began modifying carriages with an engine drive about that time, but Duryea is credited with the first successful car--one that would operate for more than very short distances. In 1896 there were estimated to be four automobiles in the entire U.S. that ran ‘reliably.’ Gasoline was available in limited quantities but demand was growing. Interestingly, the air age was also incubating, prompted by the first heavier than air flight by Wilbur and Orville Wright at Kitty Hawk, North Carolina, on December 17, 1901.

By 1901, the U.S. already needed more crude oil than Pennsylvania could provide. Then tremendous discoveries were made at Spindle Top near Beaumont, Texas, and oil quickly became a glut on the market. Historians estimate that less than 5% of the oil actually produced at the Spindle Top field reached market with millions of barrels dumped into the streams and rivers because it was not worth transporting to market. This market collapse led to the Texas Railroad Commission whose charter was to restrict oil production by ‘quotas’ on wells and fields to support prices. The refining industry shifted to Texas and the prime refinery product soon became gasoline.



Olds is credited with the first commercial auto and the first assembly line. In 1905 Olds turned out 6,300 one-cylinder Oldsmobiles. There were less than 100,000 automobiles registered in the United States by the end of that year. On the other hand, at one time there were more than 100 automobile manufacturers in the U.S.

Henry Ford is remembered both for his first car in 1896 and for his assembly line product, the Model T Ford introduced in 1908. The Model T popularity was mostly due to its low price and stout reliability. By 1910, there were 400,000 automobiles registered. By 1913, parts no longer had to be hand finished to fit Ford cars since they were interchangeable. This drove the cost down and down and forced the entire auto industry to adopt mass production of precision parts.

In 1915, motor vehicle registrations reached 2.4 million. Federal tax money for roads started flowing in 1916 with the Federal Aid Road Act. In 1919 Oregon adopted the first gasoline tax at $0.01/gallon to fund road construction.

Straight Run Gasoline for the Automobile

A market for gasoline gradually developed and it was soon sold by refiners as a finished product rather than as a nameless stock with no specifications. It was not necessary to blend the first gasoline that was sold - there was nothing to blend. The first gasoline specifications used as guidelines by refiners were primarily color (water white, an indication of purity) and density. Flash point was important because naphtha was the source of many fires. Volatility was also considered because of vapor lock in hot weather. The still operator cut *benzine*, as gasoline was often then called, using a hydrometer to establish the cut point. In time, chemical treatment with sulfuric acid primarily was introduced to remove sulfur compounds and gum formers. If more than one grade of gasoline was to be produced from the treated benzine, light and heavier gasoline were made in the batch redistillation.

Although the Octane Number as an anti-knock index was not yet a concept, it is estimated the straight run gasoline produced had an octane number in the low 60s at best and often 50 or less especially from Pennsylvania paraffinic crudes. On the other hand, automobile compression ratios were of the order of 4 and pre-ignition or knocking was not a problem.

Thermal Cracking In the 1920s Increased Production of Gasoline

The demand for automobiles and for gasoline skyrocketed after World War I ended in 1918. The outcome of that war was heavily influenced by motorized transport. After 1918, a network of roads began evolving and quickly led to more mileage driven per car. The year 1920 saw crude oil refining rates grow to 1.2 million barrels per day to feed the 9 million registered motor vehicles - nearly 4 times that of only 5 years earlier. That was roughly 5 gallons per day of refining capacity for every vehicle registered.

Refiners were faced with serious gasoline supply problems because of the relatively low 20% yield of gasoline obtained by simple distillation. More gasoline had to be produced from a barrel of crude. Thermal cracking was the solution. The Burton batch process for thermally cracking of gas oil gas was introduced in 1912 followed by Burton-Clark's improvement in surface area and capacity in 1921. Other variations evolved at the same time including the Dubbs process, the Holmes-Manley process, and the Cross process. These processes increased the gasoline yield to about 35%. The conversion of gas oil to gasoline not only increased yields but the gasoline quality and performance also improved. The cracked material didn't knock under heavy load like straight run often did and the engines produced more power. Nevertheless, despite the rapid introduction of thermal cracking, up until 1924 only 15% of the gasoline pool was cracked while the rest was straight run.

Tetra Ethyl Lead (TEL)

As automobiles got heavier, engines were first built with larger and more cylinders to provide more power. Eventually an increase in compression ratio demanded a higher quality motor fuel that did not knock under load. It was recognized that knock was related to pre-ignition or the spontaneous explosion of the entire fuel-air mix before the ignition spark. Usually caused by hot ash and deposits, it causes much higher cylinder pressures and temperatures and will often cause piston failure. Charles Kettering had developed tetra ethyl lead ($C_8H_{20}Pb$) as an anti-knock compound and had sold his lab to General Motors Chemical Company. On February 2,1923, "ethyl" anti-knock compound was introduced at the station of Refiners Oil Company in Dayton, Ohio. It was such an immediate hit that in September 1923 Standard Oil of Indiana signed the first contract for supplies of tetra ethyl lead (TEL). General Motors Chemical Company and Standard Oil formed the Ethyl Corporation in 1924. The leaded "Ethyl" gasoline contained a red dye to distinguish it from water white unleaded gasoline. Although this was done for toxicity reasons, it turned out to be a great promotional idea.

It was the introduction of TEL and the solving of odor problems that caused the rapid increase in the use of cracked gasoline. By 1926, the percentage of cracked gas jumped to 35% and then to 50% by 1940. Motor vehicle registrations reached 19 million in 1925 and refining grew to over 2 millions of barrels per day (4 gallons/day per vehicle).

But lead poisoning had been recognized for centuries and on May 26, 1926 the U.S. Surgeon General limited the amount of TEL to 3 milliliters/gallon (3.17 grams lead/gallon) of finished gasoline. This was one of the early specifications imposed upon gasoline. Still to come was a standard measure for engine anti-knock.

The Motor Octane Number

There was a great need to measure and express the various quality attributes of petroleum products. The Cooperative Fuel Research Committee, a program of ASTM, was enlisted to conduct research on problems related to fuel and fuel usage in automobiles. In 1931, the committee issued an anti-knock test procedures and described the standard test engine to be used. The method was called the Motor Method for octane determination. Motor Octane Number was considered representative of open road driving and was the principal concern at the time.

Motor octane of a gasoline was determined by running the gasoline in a standard test engine at 900 rpm and comparing the knocking tendency with blends of n-heptane and 2,2,4- trimethyl pentane. Normal heptane was declared to be zero octane. "Isooctane" 2,2,4- trimethyl pentane was declared to have an octane number of 100.

Improvements in Thermal Processes

In the 1920s and early 1930s, thermal cracking was an advanced continuous process. The old Burton and Burton-Clark batch processes were almost gone by 1930. The use of milder regimes was adopted as thermal reforming to produce aromatics. Thermally reformed naphtha had octane numbers of 70 to 90 compared to 50 for straight run naphtha. Thermal polymerization of olefinic C_3 and C_4 light ends to hexenes/heptenes/octenes also became popular.

In 1930, 24 million motor vehicles were registered and crude oil refining capacity grew to 2.35 millions of barrels per day (3.5 gallons/day per vehicle). Although registrations leveled off during the depression, they resumed their climb during the 1940s.

Chemical Engineering

With the advent of thermal cracking, there was another development. The petroleum chemist was replaced displaced by chemical engineers employing unit operations concepts to guide design and operation of refineries.

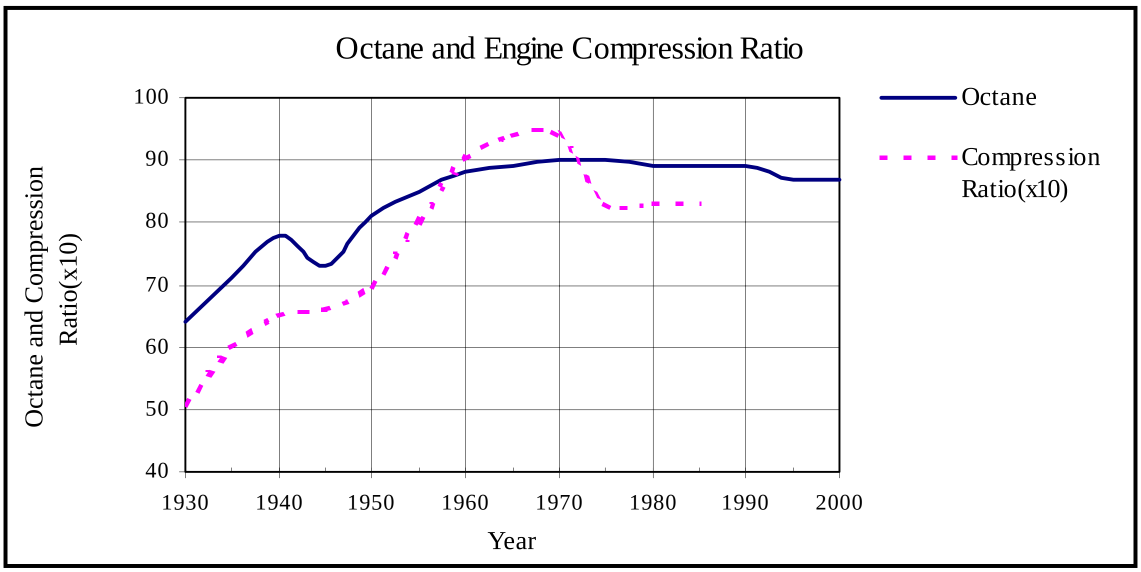
Chemical engineers were soon reducing refining art to a science, and this science was to bloom in the decades following the 1930's.

Technology permits higher performance automobiles, 1940 to 1970

At the end of World War II, the octane producing resources devoted to the war effort became available to sustain a series of engine improvements, particularly higher compression ratios, that permitted production of both heavier and more comfortable automobiles with vastly improved performance. Automobile manufacturers responded immediately to the availability of higher-octane fuels and the octane-horsepower race was on in the refining and automobile industries.

Another Anti-knock Index

Although Motor Octane Number (MON) was considered representative of open road driving, the city congestion and slow speed driving necessitated a need for another measure of low speed performance. Research Octane (RON) was measured at lower speeds. Since it typically was 5 to 10 numbers above MON and not surprising was used as a selling point in the octane race. Eventually, the average M+R/2 was adopted. For years this was known as the Pump Octane Number (PON) and also as the Road Octane Number in government publications. It is currently officially known as the Anti-knock Index.



Catalytic Processes

As part of the World War II technology development needed to make desperately needed high-octane aviation gasoline, fluid catalytic cracking, alkylation, catalytic reforming and catalytic isomerization were widely implemented. These technologies later proved to be major contributors to the octane pool for automotive gasoline.

Catalytic cracking fueled the fighters and bombers in World War II. The best grade of aviation gasoline would deliver 145% of the horsepower of 100-octane gasoline. This fuel had up to 4.6 grams/gallon of tetra ethyl lead (TEL) and was the most aircraft engines could tolerate. The planes flying from sea level airfields in India and

Burma “over the hump” of the Himalayas had to use full power of their supercharged engines. This extreme power demand with the high heat rejection loads led to destructive pre-ignition and many engine failed resulting in high losses of planes and crews as they crashed into the steeply rising terrain.

Alkylating the propylene and butylene produced from catalytic cracking added more high-octane gasoline. Catalytic reforming produces aromatics and is a major source of hydrogen for hydroprocessing.

Hydrotreating, Hydrocracking and Coking

Hydrotreating and hydrocracking have emerged to become particularly significant to the refiner. Hydrotreating is utilized on naphtha, distillates and gas oils for desulfurization and for production of higher yields of fuel products. Hydrocracking, commercialized in the early 1960s, provides flexibility for catalytic cracking to adjust product rates between gasoline, jet fuel, and diesel fuel. Plus hydrocracking can be used on feeds not suitable for catalytic cracking. Coking processes heavy residuum to produce naphtha and gas oil. Coking is especially attractive for heavy residuum that is not suitable for catalytic processes as hydrocracking or catalytic cracking.

Gasoline Manufacturing and Blending Matures

With gasoline feedstock being produced from different units in the refinery, the manufacturing and blending of gasoline became a science. Manufacturers had the option of increasing severity of reforming, adding more TEL, adding alkylate, removing normal paraffins, or isomerization normal paraffins to isoparaffins.

Aromatics fit into the higher boiling range portion of the gasoline pool, while isomerized naphtha and straight run gasoline fit nicely into the front end of the boiling curve. Economic evaluations on the optimum mix became popular. Blending into premium and regular gasoline pools differed between regions. Vapor pressure, beside octane rating, was also an important parameter. Later the phase out of TEL starting in 1975 would reduce the flexibility of blending refiners.

Gasoline Performance and Environmental Emissions Control, 1970 to 2000

Performance was historically the prime attribute for gasoline although flash fires were an early safety concern and the toxicity of tetraethyl lead (TEL) originated the addition of dye in “Ethyl” and initiated the 1926 limits for TEL in gasoline. Yet concern for other air emissions slowly strengthened.

A Brief History of Air Pollution Control

The United States has a long history of recognizing emissions as a health problem including the emissions from automobiles. Smoke was the initial early offender. Private litigation, based on nuisance common law, was the settlement method for smoke air pollution disputes prior to 1881. But the law was drifting to the conclusion that prevention of smoke was important and that legislation was a necessary tool for abatement. In 1881, the first municipal legislation was enacted in both Chicago and Cincinnati for smoke regulation. Except for the limits on tetra ethyl lead in gasoline mandated in 1926, for the next sixty-six years smoke and particulate emission abatement was the sole interest of legislation, led by Municipalities and then States.

By the middle of the 20th century the smoke problem had essentially been solved by the switch from coal to petroleum products, by efforts to increase combustion efficiency, and smoke control legislation. But it was only in 1947 that California authorized their counties to regulate air pollution other than smoke. From 1948 to 1956, widespread attention to the ill effects of air pollution were kindled by Los Angeles smog and four major episodes in Donora, Pennsylvania and London, U.K involving acute illness and approximately 5,000 total deaths. In 1955, the United States passed the first Federal air pollution law, Public Law 84-159 The Air Pollution Control Act, which authorized air pollution research and technical assistance for state and local air pollution control agencies. A series of legislation followed over the years, including The Motor Vehicle Exhaust Act of 1960 and the landmark Clean Air Act of 1963, spurred in part by several severe air pollution episodes. The Clean Air Act Amendments of 1970 formalized the technical philosophy toward air pollution control that is framework for all subsequent legislation.

Fuels Characteristics and the Impact on Refining

The composition of gasoline addresses two main issues: performance and emissions. The strategy of the manufacturer is to provide the proper gasoline composition to meet both goals. The table lists the major performance parameters of gasoline and the pollutants to be minimized. The gasoline manufacturer configures the refinery and blending streams to produce gasoline with the appropriate characteristics. The subsequent chapter *Gasoline Manufacturing Overview* covers this subject in detail.

AIR POLLUTANTS

Criteria Pollutants
- Lead (Pb)
- Particulate Matter (PM)
- Carbon Monoxide (CO)
- Sulfur Dioxide (SO2)
- Nitrogen Oxides (NOx)
- Ozone (O3)

Hazardous Air Pollutants (HAPs or Air Toxics)
- Total of 189 compounds including benzene and formaldehyde.

ENGINE PERFORMANCE

- Antiknock
- Vapor lock
- Fuel Consumption
- Engine deposits

GASOLINE CHARACTERISTICS

Emission
- Tetra ethyl lead (TEL)
- Aromatics
- Benzene
- Olefins
- Sulfur
- Oxygen
- Vapor Pressure
- T-90

Performance
- Octane
- Vapor Pressure
- Additives

GASOLINE BLENDING STREAMS

- Butane
- Isomerate (from Isomerization Unit)
- Catalytic Cracker Naphtha (“Cat Gasoline”)
- Reformate (from Catalytic Reformer)
- Alkylate (from Alkylation Unit)
- Coker Naphtha
- Visbreaking Naphtha
- Oxygenates

The development of motorized transportation has been the single most significant driving force in the growth of the petroleum refining industry. The two industries are linked together by complex interactions dealing with fuel quality. Joint studies, generically called the Auto/Oil studies, sponsored by the oil and automobile industries determined how controlling the appropriate gasoline characteristics affect performance and air pollutants. These studies also determine how the design of the automobile, with sophisticated systems for improving performance and reducing undesirable emissions, affects gasoline characteristics.

Continued growth in vehicle registration is expected to track economic growth worldwide. Petroleum fuels will remain vital and the manufacturer will continue to build refineries and produce fuels for this market.