Guest Column: *by Rick Rys*

Gasoline: Past, present and future

Part 1 of a 2 part story

It is hard not to marvel at the technical innovations of the newest BMW cars as well as some of the older models we know and love. Yet without fuel, the value of these vehicles evaporates and they are little more than pretty metal, plastic, and glass. Getting addicted to gasoline is easy. At 15 years old it was the switch from the push mower to the self propelled lawnmower that started it for me. As a mere human I am weak, but hydrocarbons can turn me into a virtual superman. I have acquired many machines that can put gasoline's energy to use.

In this first part of a two part series we will get a better idea of what gasoline is, and the forces that shape our gasoline and diesel today.

How did gasoline get here?

Some Russian geologists have speculated that hydrocarbons are a geologic entity that arrived with the formation of the earth, but the vast majority of the worlds geologists agree that Oil, Gas, and also Coal are fossil fuels that have accumulated over the past 300 million years. The stored Carbon and Hydrogen energy has its source as our Sun via photosynthesis.

It is interesting to look back, because in 1908 the first Ford Model T used Ethanol corn alcohol for fuel. At the turn of the century electric cars dominated the landscape as they were comfortable and easy to operate. Engine advances soon erased most of the advantages of the electric cars, and as gas stations appeared they gave drivers the performance and range they desired.

The gasoline and diesel fuels we use today are far more precise than they were in the early days of Gasoline. Gasoline and Diesel are complex mixtures of thousands of different molecules. The early days of Gasoline saw quite a lot of variation depending on the refiner and the source of crude oil. During World War 2 supercharged aircraft engines operated poorly on certain fuels and performance was the goal. It was during this time period that the definition for octane changed from Research Octane to Road Octane (R+M)/2 which is the simple average of the Research Octane and the Motor Octane. Each type of Octane is measured with a single cylinder Waukesha engine driven at constant speed with an electric motor. Special knock detectors compare the knock Intensity of a fuel of known Octane and to the knock intensity of an unknown fuel. Motor Octane (MON) better estimates the ability of a fuel to resist pre-combustion (knocking) under low speed, high load situations. A lot of changes occurred during this time as refining improved and additives were developed, like Tetra-Ethyl-Lead which even in very small amounts gave a large increase in Octane. The first drop of Tetra-Ethyl-Lead has an octane of about 40,000, but increasing amounts quickly reduce the octane increasing effect. Unfortunately, the Lead went out the tailpipe and accumulated on the side of the road. For those of you who drove in the 60's you may remember the white or white gray color on the inside of the tailpipe. This was a coating of lead. Unfortunately Lead is quite toxic to humans, especially infants.

> ***" ... in 1908 the first Ford Model T used Ethanol corn alcohol for fuel."***

> ***"The 1970 Clean Air Act changed gasoline forever ..."***

The 1970 Clean Air Act and gasoline

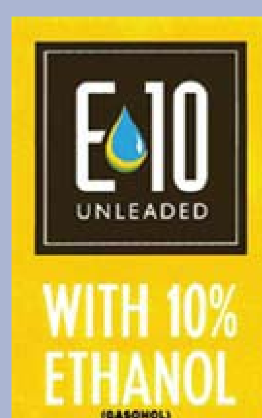
The 1970 Clean Air Act changed gasoline forever, and this act with amendments continues to change gasoline and diesel fuel. The motivating factor at the time was the unhealthy air accumulating in cities across the US. The air in all of major US cities was measured, the pollutants determined and it was up to the EPA to find a way to fix the air. Several environmental laws were enacted that put limits on industry but the EPA with help from CARB (California Air Resources Board) decided that an effective way to improve the air was to reformulate the gasoline. It was a scientific approach. There were reductions in Sulfur, limits on Benzene and Toluene, Lead was phased out, and so called Oxygenates were required to be added. Oxygenates such as Alcohols and Ethers were mandated for reformulated gasoline. Methyl tert-butyl Ether (MBTE) soon dominated and was about 15% of the gasoline. The idea with the oxygenates was to reduce the unburned hydrocarbons and reduce the carbon monoxide coming out the tailpipe.

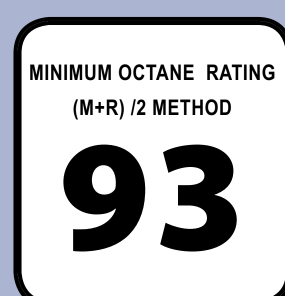
Basically the EPA strategy worked and air quality in the cities did improve as a result of gasoline reformulation. This arrangement however resulted in more than 300 different zones across the US. The construction of MTBE units at most major refineries did add a little to the cost of the fuels, but the cost of crude oil still dominates as the major factor for the price at the pump. Polluted cities were required to sell only reformulated fuels and rural areas were allowed to sell conventional (non-reformulated) fuels. In addition the gasoline vapor pressure changes 4 times a year, and is adjusted for the zone temperature and elevation.

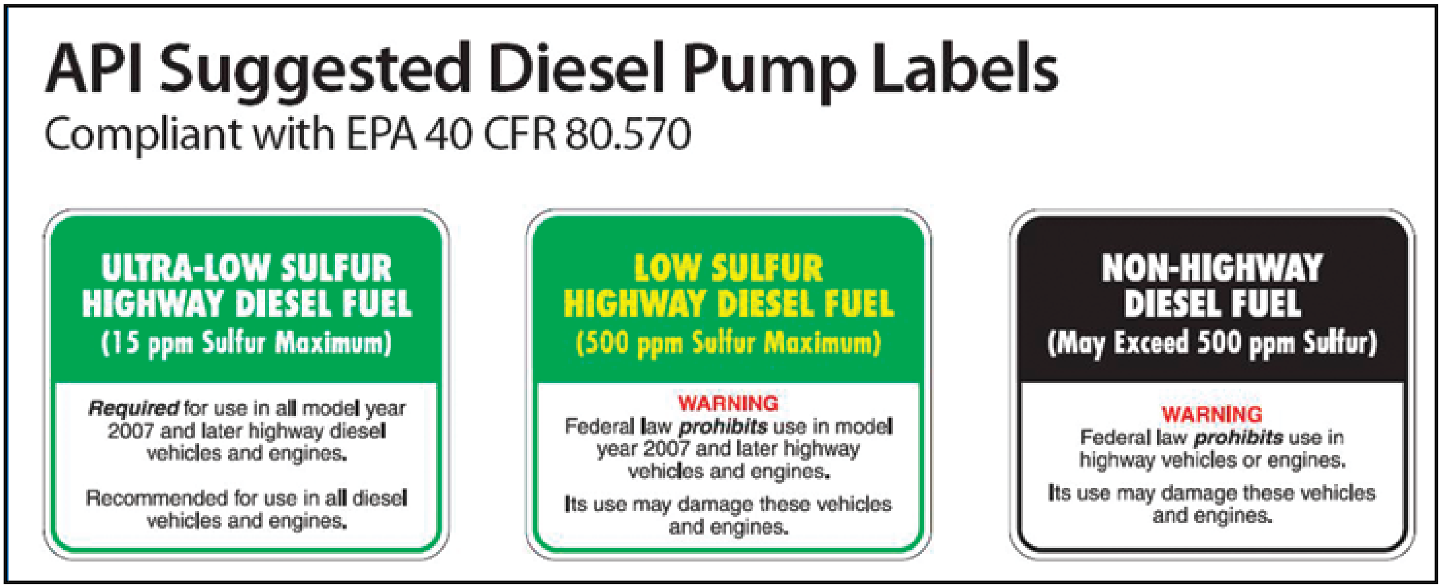
The label debate

Gasoline labels are under all kinds of debate and no real standards seem to be taking hold. In 2008 Wesley Clark proposed a country of origin label showing all countries of origin and the percentage from each country. However, this label was never widely implemented.

Most states do require some label on the ethanol content and virtually all stations post the octane because it varies with the price (see samples below).







Quality Specifications

At the refinery the gasoline must meet the following quality specification:

- ROAD - (R+M)/2
- RON - Research Octane
- MON – Motor Octane
- RVP – Reid Vapor Pressure
- Density, API Gravity
- Sulfur ppm (If your BMW Nikasil engine has made it to 2006, it will survive)
- Aromatics Vol%
- Olefins Vol%
- Weight percent Oxygen
- NOX Nitrous Oxide reduction by Region
- TOX Toxic Air pollutants by region
- VOC Volatile Organic Compounds by region
- T10 Temperature at which 10 % is evaporated. ASTM Distillation
- T50 Temperature at which 50 % is evaporated. ASTM Distillation
- T90 Temperature at which 90 % is evaporated. ASTM Distillation
- FBP Final Boiling Point
- E200 Volume % evaporated at 200 °F
- E300 Volume % evaporated at 300 °F
- DI Drivability Index
- VLI Estimate of the temperature at which the Vapor-Liquid ratio is 20

Unlike the MTBE of old, ethanol dissolves sludge in pipelines and storage tanks, so it is not blended at the refinery, and is instead blended in the distribution system. As such oxygen content regulations are being replaced with a simple E10 or 10 volume percent ethanol.

Diesal labels

The API recommended Diesel labels are shown in the figure above. It is interesting that the Cetane of the fuel is not posted, and it is unlikely the clerk behind the counter has any clue what it actually is. The key specifications that the refinery blends diesel are:

- Cetane
- CFPP - Cold Filter Plug Point
- CLOUD - Cloud Point
- Flash - Flash Point
- Density, API
- REC250 Volume % distilled at 250 DegF
- REC350 Volume % distilled at 350 DegF
- S – Sulfur PPM Wt
- T10 Temperature at which 10 % is evaporated. ASTM Distillation
- T20 Temperature at which 20 % is evaporated. ASTM Distillation
- T50 Temperature at which 50 % is evaporated. ASTM Distillation
- EndPoint - ASTM Distillation
- VISC20 – The viscosity at 20° C. according to ASTM D445
- VISC40 – The viscosity at 40° C. according to ASTM D445

US takes the lead

In the 1990s the US took the lead in reformulating fuels and removing the lead. Europe, Asia, and Latin America followed our lead. More recently the Europeans have made cleaner fuels than the US, for example the European Sulfur content was much lower than US Diesel since 2005 (50ppm vs. 500ppm in the US) and was made even lower in 2009 (10ppm vs. 15ppm in the US). Also European Gasoline's typically have higher octane's than the same grade of US Gasoline and higher cetane than the same grade of US Diesel. Sweden markets a Diesel fuel called EcoPar that has no sulfur. Shell has developed a process that can convert Natural Gas to sulfur free diesel.

Rick Rys took this picture while working at a refinery in Venezuela. The large yellow piles are sulfur that was removed from crude oil.

Protecting ground water

During the mid-'90s, it was noticed that widespread contamination of ground water with MTBE was taking place in many states, with California reporting 5 to 10 % of its drinking water sources having detectable levels of MTBE. By 2006 MTBE was out and Ethanol was in with some drop in gasoline energy content. Both MTBE and Ethanol had high octane, but the higher amount of oxygen in the ethanol allowed a reduction from 15% MTBE to 10% Ethanol. The laws mandating and subsidizing ethanol were much more political than scientific as unlike reformulated gasoline no specific environmental benefits were ever predicted for ethanol. Even with the high gasoline prices in 2006, producing a gallon of ethanol cost more than 38 cents per gallon more than making gasoline with the same energy content. Corn ethanol subsidies in 2006 totaled $7 Billion dollars for 4.9 billion gallons of ethanol. That is about $1.45 per gallon. Current legislation is being debated to extent those subsidies and tax cheaper Brazilian ethanol.

In 2008 the US saw a big reduction of Sulfur in Gasoline from about 400ppm to 30ppm. Some may remember the BMW recall of certain Nikasil engines. BMW replaced these with the more sulfur resistant Alusil engines. It was the Sulfur in the US gasoline that caused the engine failures in the US when such failures did not happen in Europe. When sulfur goes through the engine it is converted to sulfuric acid. Short trips allowed water to condense on the cylinder walls and sulfuric acid with the water present caused corrosion of the cylinder walls leading to oil consumption problems. If your Nikasil engine is still alive today the low sulfur fuels we now have in the US will greatly reduce the sulfuric acid corrosion problem.

> ***"BMW replaced these [Nikasil engines] with more sulfur resistant Alusil engines."***

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The cost for removing sulfur from gasoline and diesel is in the range of 3-5 cents per gallon. Removing sulfur has no impact on the energy content, Octane or Cetane.

The NOx problem

NOx is another important pollutant formed by gasoline engines but NOx is a bigger problem with Diesel engines due to the higher combustion temperatures. NOx is formed by Nitrogen in the air reacting with oxygen in the air. NOx in the tailpipe combines with water to form Nitric Acid and is a major factor in smog. The EPA requirement to reduce NOx emissions starting in 2009 was ironically related to the delayed availability of diesels for passenger cars. It was the sulfur in the diesel fuel that caused this delay. The auto companies were actually fighting for stricter sulfur limits while the API (American Petroleum institute) was fighting against them. In 2009 the Sulfur in US diesel fuel dropped from 500ppm (LSD or Low Sulfur Diesel) to 15 ppm (ULSD or Ultra Low Sulfur Diesel). ULSD is now carried by 99% of all gas stations in the continental US states. Alaska however has not made the transition to ULSD. Sulfur in the exhaust disturbs most technologies for reducing NOx. Sulfur poisons the catalysts used for NOx treatment and reduces the effectiveness of Urea injection. Power plants routinely inject NH_3 (Ammonia) into the flue gas to reduce the NOx emissions. This same technique is used in the exhaust of the modern Diesels but using the chemically similar Urea instead.

The new exhaust systems

Take a careful look at the exhaust system on a 2009 or newer diesel car and you no longer see just a muffler, but up to 4 separate catalyst beds, O2 and Temperature sensors, and maybe a back pressure control valve. Mercedes, BMW, and Audi have chosen to inject Urea for NOx control. In 2009 VW TDI engines managed to meet the NOx requirements and the strict Tier II Bin 5 requirements without the need for Urea injection. All of the new Diesel cars trap the particulates (soot) and periodically burn it off. Interestingly light trucks are not required to meet the same requirements. It was possible to buy Diesel trucks and SUV's in 2007 and 2008 while diesel cars were not available.

"All of the new Diesel cars trap the particulates (soot) and periodically burn it off."

The EPA Phase 3A requirements cover the period from 2010 to 2016. In summary, fleet mileage for cars will have to average 42 mpg, and trucks will have to average 26 mpg by 2016. So we are seeing a shift from regulations based on traditional air pollutants with more emphasis on general efficiency.

In the second part of the series we will look at some of the future production and environmental pressures on hydrocarbons, discuss a little about the future of Biofuels, and discuss the competition for more fuel efficient engines including the competition with electric motors. ♦

Editor's Note: Rick Rys is a BMWCCA and BMW-MOA member. He is a registered chemical engineer (MA). He worked for Foxboro Company for 20 years, but has run his own consulting engineering company for the past 13 years. He developed equipment, software, and control systems to manufacture and blend gasoline and diesel fuel at many oil refineries worldwide. At Foxboro he developed gasoline and diesel blending systems that helped refineries meet the EPA and CARB requirements for reformulated gasoline.