Gasoline Quality

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In this article, the author hopes to accomplish four objectives: provide a primer on gasoline, discuss the origins of gasoline contaminants and their removal, provide information on the effect of contamination on dispensing components, and discuss the gasoline properties to consider in choosing which grade of gasoline to purchase.

Gasoline Properties

Gasoline is a mixture of hydrocarbons distilled from crude oil containing specified maximum levels of impurities and some minimum level of performance-enhancing additives. The overall characteristics of the blend were traditionally defined by an allowable maximum vapor pressure and a performance index called an octane number. In recent years, efforts to reduce air pollution have extended these definitions to include restrictions on the chemical composition of gasoline blends.

In a typical gasoline engine, a pre-mixed charge of fuel and air is admitted into a cylinder, compressed, combusted and exhausted. The exhaust constituents depend on the completeness of the combustion, which is influenced primarily by engine design, but to some degree by gasoline composition. Complete or stoichiometric combustion of a fuel, including gasoline, results in carbon dioxide and water as by products:

$$C_xH_y + (x + \tfrac{y}{4})\, O_2 \rightarrow xCO_2 + \tfrac{y}{2} H_2O$$

Since air is used as the primary source for oxygen, secondary reactions occur between nitrogen and other species under the extreme conditions inside the cylinder. Additionally, trace impurities and other incomplete combustion products contribute to the emission of volatile organic carbons, or VOCs.

The majority of the 200-some gasoline components are alkanes, i.e. saturated hydrocarbons, with 4 to 12 carbon atoms. The balance of gasoline consists of unsaturated hydrocarbons, alkenes, akynes or olefins, all of which are less stable than alkanes, and some polynuclear aromatics (PNAs) which are high boiling, unstable, and the source of some residues and gums.

In 1995, nine metropolitan areas were required to switch to reformulated gasolines (RFGs) for VOC controls. RFG requirement resulted in limits on benzene, sulfur, and aromatics, to achieve reductions in VOC, NOx and toxics emissions. In addition, oxygen content of at least 2.0% by weight was required to improve cold-start emissions from older cars and, according to some, reduce the reactivity of emitted VOCs.

In order to increase the fuel's oxygen content the oil industry uses alcohols and ethers, both of which boost the octane rating, which was lowered with lower aromatics limits. Ethanol and methyl tertiary butyl ether (MTBE) are the primary oxygenates, with tertiary amyl methyl ether

(TAME) and ethyl tertiary butyl ether (ETBE) used in limited quantities. Recently publicized environmental problems with MTBE may restrict its future use as an oxygenate.

Gasoline specifications are set by regulatory agencies and must conform to industry standards established by ASTM D4814. These specifications ensure that evaporative emissions and driveability parameters are met by specifying volatility, define combustion characteristics through octane ratings, maximize product stability and minimize its corrosiveness.

Volatility Properties include vapor pressure, distillation curve, and driveability index properties with the objectives of controlling startability, evaporative emissions, and cold-start/warm-up performance emissions.

Antiknock Index (Octane) defines the resistance to auto-ignition or knocking in an engine. There are two methods of determining the index, motor octane (MON) and research octane (RON); the posted octane, here in the United States, is the average of the two. The octane rating scale is defined by two compounds: iso-octane (C_8H_{18}) which is extremely resistant to auto-ignition and assigned a RON and MON of 100, and n-heptane (C_6H_{16}) which is highly susceptible to self-ignition and assigned an octane of zero. A gasoline blend exhibiting the same knock properties as a mixture of 90% iso-octane and 10% n-heptane would have an octane rating of 90. Since isooctane is the reference at 100, it is possible to have octane ratings greater than 100 for fuels that have greater resistance to auto-ignition, such as most aromatics, alcohols and ethers. In Europe, octane postings appear higher than here since RON rather than an average of MON and RON is used.

The oil industry has done significant work on engine octane requirements. When new, engines generally run well on the fuel recommended by the manufacturer. However, as engines age and experience combustion chamber deposits (CCDs), they also experience an increase in octane appetite, known in the industry as ORI, or Octane Requirement Increase.

Maximum Solvent Washed Gum provides a limit to non-distillable residue.

Copper Strip Corrosion measures the ability for gasoline to tarnish copper and is an indicator for potentially corrosive sulfur compounds which could corrode the fuel system.

In addition, there are specifications for maximum *sulfur* and *lead* contents in order to minimize air toxics and corrosive components.

Gasoline Distribution

The great majority of gasoline today is blended at refineries to either regular or premium specifications and shipped to distribution terminals via pipelines or on barges. From the terminal, it is delivered via tank truck to the service station. If ethanol is used as the oxygenate, it may be blended at the terminal truck rack during loading. If the station uses blending dispensers, only regular and premium products are delivered; the mid-grade product is blended at the dispenser. Older stations, with non-blending three-product dispensers will have all three products delivered, with mid-grade gasoline blended at the terminal.

Most gasoline is fungible; a terminal may supply the same base gasoline to different branded outlets, while differentiating the performance by blending the specific brand's detergent additive package at the truck rack. Terminal rack blending operations have become quite sophisticated, in providing automated additive injection and data logging for many different additives. Prior to loading into tankers, the product may be filtered to minimize contaminants. Some major oil companies routinely filter gasoline delivered to stations.

At the station, product is generally dropped into underground storage tanks. Each tank contains a submersible pump which delivers the specific product to each dispenser. The final quality assurance step is a cartridge filter for each product in most dispensers at service stations. These filters are designed to minimize the possibility of water and solids reaching a vehicle tank.

Gasoline Contamination
Most of us have experienced or know someone who has experienced driveability problems which can be related to the fuel. A recent example is that of a major oil company delivering regular gasoline contaminated with fuel oil to several stations during cold Midwestern winter days. The results were serious driveability problems for many customers. This type of problem is very rare and usually isolated to a small area; however, more frequent problems result from water or solids reaching a customer's vehicle tank.

Product contamination may actually start at the refinery. A number of refinery processes use acid catalysts and require a neutralization step which may result in occasional carryover of caustic. In addition, final polishing or "sweetening" processes used to remove high boiling contaminants also use caustic to remove residual catalysts. If small amounts of caustic are carried over into the product, they may react with other gasoline components or additives and form solids which can appear as gray/black particles, waxy slime which deposits on dispenser filters, or other types of solids.

Shipping products via barges or pipelines can also result in contamination. Barge compartments are generally fabricated of steel. The humid environment can cause rust when empty. Additional problems may occur when ballast water is admitted to the product compartments for leveling the vessel and not properly removed. Pipelines experience occasional settling of solids within the pipeline. When pressure drops increase, operators may send a solid plug, known as a pig, up the pipeline in order to remove the obstruction. The fate of contaminants produced depends entirely on the amount of care exercised when cutting product streams at the nearest terminal tank.

A different set of problems manifests itself as a source for contaminants at terminals. Most terminal tanks today are large diameter steel vessels with floating roof tanks. When a roof is down, the steel walls above are exposed to the atmosphere and rust. Water from condensation or leaks may also accumulate on the floating roofs. The edges of the roof are sealed to the side wall via seals made of fuel resistant materials. As the roof moves up and down, small particulates are formed from abraded seal material, rust and water and find their way into the product.

The last area for creating contamination is the station storage tank. Steel tanks may experience rust formation in the vapor space. Particulates may also enter through drain valves in spill buckets. In warmer climates, soil particulates may introduce microbes into the tank, which may thrive in the water/ product interface and produce additional contaminants. Product delivery into station tanks is via drop tubes to the bottom of the tank, providing vigorous agitation during each delivery. If contaminants are present they may experience sufficient shear to form emulsions with long settling times.

Removing Gasoline Contaminants

Having discussed various scenarios for contaminating gasoline, how can oil companies and station owners/operators ensure that their customer is receiving a quality product? The answer is, of course, somewhat obvious: attention to detail by eliminating the source whenever possible or the contamination if the source cannot be eliminated. Little can be done about the particulate generation process in terminal tanks. However, the product can be filtered prior to loading into tank trucks. Periodic cleaning of tanks and tank bottoms water management can minimize the problem. At the station, attention to detail is again the key to success. Keeping spill buckets clean and periodically cleaning tanks will minimize contamination. The last line of defense is the dispenser filter, which must be maintained and changed periodically to ensure high flow rates and continued customer satisfaction. Something which should never occur is that an owner/operator of a station replace filter cartridges with blanks if repeated filter plugging occurs. An alternative to dispenser based filtration is the installation of larger filter units at the submersible pump.

Equipment Problems

If contaminants are allowed into the dispenser piping, serious problems are inevitable. The most immediate problem is the potential of plugging a customer's fuel filter or injectors. However, at the station contamination can manifest itself in other equipment failures which may become expensive to repair and can affect the station's safe operation.
One of the more expensive items to repair or replace in a dispenser is the product meter. Depending on the degree of contamination, its operation may become erratic or it may stop working.

The effect of contaminants on hanging hardware, i.e. hoses, nozzles and breakaways, are less predictable. The potential of coating inside surfaces with deposits may lead to corrosion and pitting of the surfaces, especially if they are aluminum. In the extreme, serious contamination may result in failure of some components. The author has seen breakaways fail open rather than closed and nozzles that fail to shut off.

During the last two years, the Petroleum Equipment Institute documented about a number of vehicle fires resulting from static discharge during fueling. While direct links between contamination and static discharge have not been established, inspection of failed components suggests that contaminant induced surface coating and corrosion may have been responsible for reducing the conductivity of affected components. The Institute has issued RP400-2, a Recommended Procedure for Testing Electrical Continuity of Petroleum Dispensing Systems.

Which Grade Gasoline?

This question has always been of great interest to the consumer who has little basis for his choice other than advertising and old wive's tales. Let us start by stating that today's engines are much different than those built decades ago. Modern engine management systems today rely on more computing power than most of the Apollo Space Program, with an objective of minimizing exhaust pollutants and evaporative losses. Tailpipe and crankcase losses have been reduced by about 99% of their unregulated levels in the 1960s. In fact, ultra low emissions vehicles, or ULEVs, emit less than 0.3% VOC of the preregulation era.

With the increased sophistication of modern engine management systems, comes the ability to effectively utilize a wide range of fuels. Knock sensors are used by the engine to retard timing should the engine experience knock burning fuels with insufficient octane ratings. Engine power can be reduced by the intervention of the knock sensor, but the reduction is usually brief. Under this scenario, regular gasoline will suffice for most vehicles. High-performance engines for which the manufacturer recommends premium fuel will generally not be damaged by the use of regular, but the loss of power and corresponding acceleration performance can drop by 5% or more when the premium octane requirement is not met.

With many gasoline quality parameters regulated, the obvious question is if there is a difference among gasoline brands. The answer is a resounding yes. Differentiation is achieved through proprietary additive packages which contain anti-oxidants, metal deactivators, surfactants, deposit modifiers, corrosion inhibitors, and, of course, octane enhancers. In addition, gasoline retailers vary significantly in the level of care taken to prevent contamination; some companies have specific quality control procedures and special equipment to avoid contamination, while others do not.

While all of us have suffered through countless television ads claiming superior performance for particular gasolines, the reality is that those claims must be backed by substantial test data in order to meet the Federal Trade Commission (FTC) advertising requirements. While there has been a debate concerning the value of premium gasolines in engines that really do not need them (which is the majority of today's engines), the facts are that major brand premium gasolines generally contain higher dosages of premium additives designed to reduce intake valve deposits, spark plug fouling and keep fuel injectors clean. A number of major oil companies have demonstrated that their additive packages reduce emissions, have the ability to restore engine performance and most take extra care in ensuring that their premium product exceeds customer expectations.

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