MEMORANDUM

SUBJECT: Water Phase Separation in Oxygenated Gasoline
- Corrected version of Kevin Krause memo

FROM: David Korotney, Chemical Engineer
Fuels Studies and Standards Branch

TO: Susan Willis, Manager
Fuels Studies and Standards Group

On May 26, 1995, Kevin Krause finalized a memorandum describing the conditions under which water phase separation will occur in oxygenated gasolines. Recently, several errors were discovered in that memorandum. I have made the necessary corrections, and now resubmit the complete text of Kevin's memo for your review and approval.

Introduction

With the introduction of oxygenated gasoline came the concern of water phase separation. Water in gasoline can have different effects on an engine, depending on whether it is in solution or a separate phase, and depending on the type of engine being used. While separate water phases in a fuel can be damaging to an engine, small amounts of water in solution with gasoline should have no adverse effects on engine components. If precautions to prevent water from entering the fuel system are taken, water phase separation will likely not occur.

Discussion

Oxygenated fuels usually contain either ethanol or methyl-tertiary-butyl-ether (MTBE). Other possible oxygenates include ethyl-tertiary-butyl-ether (ETBE), tertiary-amyl-methyl-ether (TAME), and tertiary-butyl-alcohol (TBA). Chemically, ethanol and MTBE behave differently. Ethanol, for example, will readily dissolve water, and is considered infinitely soluble in water. MTBE, on the other hand, has little affinity for water, and can only be dissolved in water to a content of 4.3 volume percent (at room temperature). Therefore, ethanol/gasoline blends can

dissolve much more water than conventional gasoline, whereas gasoline/MTBE blends act very much like conventional gasoline when in the presence of water.

Since ethanol and water readily dissolve in each other, when ethanol is used as an additive in gasoline, water will actually dissolve in the blended fuel to a much greater extent than in conventional gasoline. When the water reaches the maximum amount that the gasoline blend can dissolve, any additional water will separate from the gasoline. The amount of water required (in percent of the total volume) for this phase separation to take place varies with temperature, as shown in Figure 1. As an example, at 60 degrees F, water can be absorbed by a blend of 90% gasoline and 10% ethanol up to a content of 0.5 volume percent before it will phase separate. This means that approximately 3.8 teaspoons of water can be dissolved per gallon of the fuel before the water will begin to phase separate.

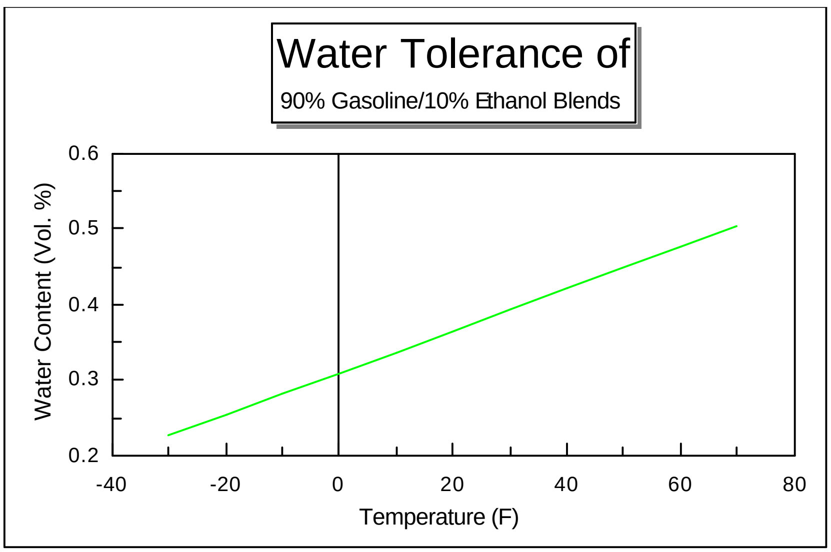

Figure 1

Since MTBE has much less affinity for water than does ethanol, however, phase separation for MTBE/gasoline blends occurs with only a small amount of water, as shown in Figure 2. A blend of 85% gasoline and 15% MTBE can hold only 0.5 teaspoons at 60 degrees F per gallon before the water will phase separate. For comparison, one gallon of 100% gasoline can dissolve only 0.15 teaspoons water at the same temperature. These figures are far below the 3.8 teaspoons which will cause phase separation in the 90/10 ethanol blend.

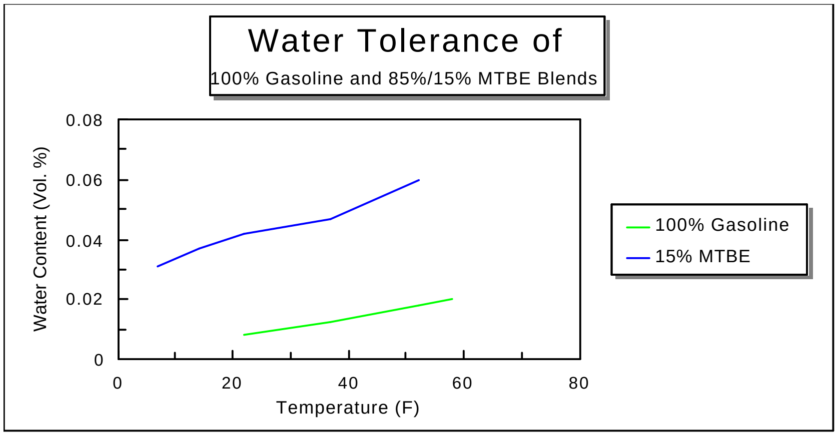

Figure 2

Water can enter gasoline engines in two ways: in solution with the fuel or as a separate phase from the gasoline. Water in solution operates as no more than an inert diluent in the combustion process. Since water is a natural product of combustion, any water in solution is removed with the product water in the exhaust system. The only effect water in solution with gasoline can have on an engine is decreased fuel economy. For example, assuming a high water concentration of 0.5 volume percent, one would see a 0.5 percent decrease in fuel economy. This fuel economy decrease is too low for an engine operator to notice, since many other factors (such as ambient temperature changes, wind and road conditions, etc.) affect fuel economy to a much larger extent.

Water as a separate phase, however, can have differing effects on gasoline engines, depending on whether the engine is two-stroke (generally, smaller engines) or four-stroke (generally automobile engines). In the case of conventional and MTBE-blended gasolines, when a water phase forms, it will drop to the bottom of the fuel tank, and can therefore be drawn into the engine by the fuel pump. Therefore, large amounts of water will prevent the engine from running, but no engine damage will result.

Phase separation in ethanol-blended gasoline, however, can be more damaging than in MTBE blends and straight gasoline. When phase separation occurs in an ethanol blended gasoline, the water will actually begin to remove the ethanol from the gasoline. Therefore, the second phase which can occur in ethanol blends contains both ethanol and water, as opposed to just water in MTBE blends and conventional gasoline. In the case of two-stroke engines, this water-ethanol phase will compete with the blended oil for bonding to the metal engine parts. Therefore, the engine will not have enough lubrication, and engine damage may result. In the case of four-stroke engines, the water-ethanol phase may combust in the engine. This combustion can be damaging to the engine because the water ethanol phase creates a leaner combustion mixture (i.e. air to fuel ratio is higher than ideal). Leaner mixtures tend to combust at higher temperatures, and can damage engines, particularly those without sensors to calibrate air to fuel ratios.

Phase separation, however, generally only occurs when liquid water (as opposed to water vapor) is introduced to the fuel system. If tank vents are left open, either in the engine being operated, or at a fuel distribution station, water can enter the fuel system in the form of rain (or spillage, etc.) or through the air in the form of moisture. Also, since conventional gasoline absorbs very little water, there is often a layer of water present at the bottom of a filling station tank normally used to store conventional gasoline (water is more dense than gasoline, and will therefore sink to the bottom). Before an oxygenated gasoline is added to such a storage tank for the first time (particularly ethanol-blended fuels), this water must be purged from the tank to prevent the water from removing any ethanol from the fuel.

Since the solubility of water in both gasoline and air decreases with a decrease in temperature, water can enter a fuel system through condensation when the atmospheric temperature changes. For example, assume a tank containing conventional gasoline contains only one gallon of fuel. Assume also that it is closed while the outside temperature is 100 degrees F with a relative humidity of 100 percent. If this tank is left sealed and the temperature drops to 40 degrees F, water will likely condense on the inside of the tank, and dissolve in the fuel. In order for enough water to condense from the air to cause gasoline-water phase separation, however, there must be approximately 200 gallons of air per gallon of fuel over this temperature drop (100 to 40 degrees). Since oxygenated fuels can hold even more water than conventional gasoline, it is even more unlikely that enough water will condense from the air to cause gasoline-water phase separation.

Another way water can enter gasoline is through absorption from the air. Water, in the form of water vapor, can dissolve in gasoline. The more humid the air, the faster the water vapor will dissolve in the gasoline. Due to chemical equilibrium, however, assuming a constant temperature, phase separation will never occur if the only source of water is from the air. Only enough water to saturate the fuel can enter the system, and no more. Water vapor, however, dissolves in gasoline very slowly, even at very high humidity. For example, at a constant temperature of 100 degrees F and relative humidity of 100%, it would take well over 200 days to saturate one gallon of gasoline in an open gasoline can (assuming the only source of water is water vapor from the air). Water absorption from the air is far slower at lower temperatures and humidities. (At a temperature of 70 degrees and relative humidity of 70%, it would take over two years to saturate one gallon of conventional gasoline in the same gasoline can.) Again, oxygenated gasolines can hold more water than conventional gasoline, and would therefore take much longer to saturate with water.

Conclusion

Water phase separation in any gasoline is most likely to occur when liquid water comes in contact with the fuel. (Water in the form of moisture in the air will generally not cause phase separation.) Water which is in solution with gasoline is not a problem in any engine, but as a separate phase it can prevent an engine from running or even cause damage. Since oxygenated gasolines, however, can hold more water than conventional gasoline, phase separation is less likely to occur with oxygenates present.

For any gasoline, simple precautions to prevent phase separation from occuring should be taken. First of all, gasoline should not be stored for long periods of time, especially during seasonal changes which usually have large temperature changes associated with them. (For both oxygenated and conventional gasolines, gumming can also occur which is detrimental to any engine.) If it is unavoidable to store gasoline for a long period of time, one should be sure that the tank if full to prevent condensation of water from the air, and the addition of a fuel stabilizer should be considered. Lastly, care should be taken not to allow water into the fuel sytem while filling fuel tanks or operating the engine -- in the form of rain or a spash, for example.

References

"Alcohols and Ethers: A Technical Assessment of Their Application as Fuels and Fuel Components." API Publication #4261, July 1988.

Douthit, W.H., B.C. Davis, E.D. Steinke, and H.M. Doherty. "Performace Features of 15% MTBE/Gasoline Blends." SAE Technical Paper Series #881667, October 1988.

"Fuel Ethanol." Technical Bulletin, Archer Daniels Midland Company, September 1993.

"Storing and Handling Ethanol and Gasoline-Ethanol Blends at Distribution Terminals and Service Stations." API Recommended Practice #1626, First Edition, April 1985.

"The Use of Oxygenated Gasoline in Lawn & Garden Power Equipment, Motorcycles, Boats, & Recreational Equipment." Downstream Alternatives, Inc. Document #941101, November 1994.

"Use of Oxygenated Gasolines in Non-Automotive Engines." Chevron Technical Bulletin, December 1992.