Is Ethanol a Good Replacement for MTBE?

Methyl tertiary butyl ether (MTBE), an oxygenate in gasoline, is expected to be banned in all states in the near future. What will replace MTBE? Probably ethanol (ethyl alcohol). Ethanol has been used in gasoline for several years. However, as Sullivan D. Curran, PE and Armin E. (Gene) Mittermaier, PE discuss, its potential use on a broader scale has heightened concerns of the experts about its compatibility and permeability, and its related efforts on gasoline driven engines and petroleum equipment.

Compatibility and permeability issues
Many states have passed or are considering legislation banning the use of methyl tertiary butyl ether (MTBE) as an oxygenate in gasoline. A strong candidate for replacing MTBE is ethanol (ethyl alcohol), which is produced mainly from grain or sugar. While ethanol has been used in gasoline for several years, its potential use on a much broader scale has heightened concerns about its compatibility with storage and distribution system components and its potential harmful effects on gasoline-driven engines. While much needs to be done to fully assess these issues, this article presents information on what is known today about ethanol’s compatibility with equipment and engines.

Efforts have been launched by the New England Interstate Water Pollution Control Commission (NEIWPCC) and the American Petroleum Institute (API) to study the compatibility and permeability of ethanol blended fuels with underground storage systems including dispensers, pumps, fuel monitoring systems, piping and tanks. These initial efforts are focused on database searches for available information to be used in evaluating the multi-media environmental impacts of ethanol as the possible oxygenate in fuel supplies due to the methyl tertiary butyl ether (MTBE) backlash.

Ethanol-gasoline blends have been in use for more than 20 years, but largely since the 1970s. In April 1985, API reported that “the use of ethyl alcohol (ethanol) as a motor fuel component has increased significantly in recent years.” However, since the 1985 API report (i.e., API Recommended Practice 1626, Storing and Handling Ethanol and Gasoline-Ethanol Blends at Distribution Terminals and Service Stations), the industry has gained 15 years of additional experience using established materials, and more recent experience with new materials. While NEIWPCC and API plan to report their findings in 2001, this paper addresses much of the relevant documentation that we are currently aware of.

MTBE versus ethanol
The thrust of the NEIWPCC and API studies is to evaluate the potential effects of changing reformulated gasoline oxygenates from MTBE to the most common alternative, ethanol. In January 1999, Shell Oil Company submitted to the State Water Resources Control Board’s Advisory Panel a
paper entitled Compatibility and Permeability of Oxygenated Fuels to Materials in Underground Storage and Dispensing Equipment. This public document made summary observations including the following comparisons between MTBE and alcohol blended fuels:

**MTBE blended fuels**
- “From a metals corrosion viewpoint, gasoline is a rather benign liquid and MTBE does not increase the corrosiveness of the hydrocarbon blend.”
- “From a polymer compatibility viewpoint, neat MTBE is an aggressive swelling agent for some, but not all, polymers. (MTBE is not an aggressive swelling agent for thermoplastic polymers.) At 15 percent concentration in gasoline, the effects of MTBE do not compromise equipment integrity.”
- “Permeation of gasoline through composite materials typical of fiberglass tanks, rigid piping and sumps has not been observed despite two reported attempts to measure it.” (While this statement may suggest to the reader that permeation through fiberglass is unmeasurable, there are test methods that will measure its permeability, as discussed later under “Piping.”) “Permeation of reformulated gasoline through thermoplastic and elastomeric materials typical of flexible hoses and piping has been observed.

**Alcohol blended fuels**
- “Conversely, the corrosive nature of alcohol blended fuels with regard to metals and polymers alike is well documented.”
- “Absorption and permeation of alcohol blended fuels in and through polymeric materials are observed to be of considerably greater magnitude than that observed for ether (e. g., MTBE) blended fuels.”
- “Alcohols, particularly methanol, produce more excess permeation than does MTBE.”
- “The electrical conductivity of hydrated fuel is increased to the point where galvanic and electrolytic corrosion may be enabled.” (Ethanol-gasoline blends can dissolve and hold in suspension as much as 24 times more water than MTBE-gasoline blends.)

In summary, there are numerous compatibility and permeability issues associated with the use of ethanol that are relatively benign when MTBE is used as an oxygenate. These issues warrant further discussion.

**Ethanol**
Ethanol or ethyl alcohol (C2H5OH) is primarily produced from grain or sugar by a fermentation process. The National Energy Act of 1978 provided a federal tax exemption of six cents per gallon for blends of agriculturally-based ethanol. Some states grant tax waivers averaging 3 cents per gallon. Consequently, many areas have not used MTBE as the oxygenate of choice. The principal advantages of ethanol as a fuel are its high octane and reduction of carbon monoxide emissions from older model
vehicles. The principal disadvantages include:

- High blending vapor pressure. The EPA gasohol waiver for alcohol-gasoline blends does not limit the RVP as it does for other oxygenated fuels. Thus, the use of gasohol fuel results in higher vehicle evaporative emissions.

- Low energy density. Ethanol’s BTU content is two-thirds that of gasoline.

- Tendency to phase-separate with water in mixtures with gasoline. The tendency to phase-separate is why ethanol is blended at marketing terminals rather than at the refineries and shipped via pipeline or marine vessels.

- Corrosivity and moderate solvency of certain plastics and gasket materials. Corrosivity and moderate solvency are the reasons gasohol may dislodge rust, gum and sediments if present in storage, handling and automotive fuel systems.

- Ethanol toxicity. Ethanol is a central nervous system depressant and moderately toxic to humans. However, it is much more toxic to lower species.

As discussed next, the tendency of ethanol to phase-separate with water can cause significant harm to gasoline engines and storage and handling components.

**Ethanol-gasoline and water**

Water can enter the fuel through absorption from the air (via the diurnal breathing of atmospheric storage systems) or by unintended introduction during the distribution, storage and transfer operation. Water will dissolve, to a limited degree, in an ethanol-gasoline blend.

For example, at 60° F, water can be absorbed by a blend of 90 percent gasoline and 10 percent ethanol up to a content of 0.5 percent (volume) before it will phase-separate. This means that 12 teaspoons of water can be dissolved per gallon of the fuel before the water will begin to phase-separate.

When a water phase forms, it is heavier than the gasoline blend and drops to the bottom of the fuel tank. If allowed to reside in the tank bottom, the water phase will attract certain gasoline additives and ethanol. In other words, some of the additives (e. g., detergents) and ethanol in the gasoline will move to the water phase. In sufficient quantities and concentrations, this water-additive-ethanol phase has the potential to adversely affect vehicle engines and storage and handling system components.

**Compatibility and permeability**

The compatibility and permeability issues with regard to the use of ethanol as the replacement for MTBE affect the equipment and components that come in contact with the fuel. These include the gasoline engines that will be powered by the fuel and the system components used in the storage and distribution of the fuel, including dispensers, pumps, fuel monitoring systems, hoses, nozzles, swivels, piping and tanks. Each of these deserve specific analysis and consideration, as indicated by the
following facts.

**Gasoline engines**

**Vehicle population:**
The latest complete state motor vehicle statistics show that there were approximately 206.6 million vehicles registered in the US during 1997. Vehicle population turnover occurs over 20+ years. Therefore, even if flexible fuel vehicles were mandated, traditional gasoline-consuming vehicles will dominate well into the future.

**Manufacturer warranty:**
A survey of 24 automobile manufacturers’ vehicle engine warranty conditions show that they require the alcohol level in alcohol-blended gasoline to not exceed 10 percent. Higher concentrations used in some vehicles may cause poor cold engine performance, most notably stalling, rough idling and hesitation. Also, these higher concentrations may lead to high valve train wear and the deterioration of elastomers and non-ferrous metals. As a result, the EPA’s allowable limit for ethanol in gasoline is 10 percent.

**Engine Damage:**
In the case of two-stroke engines (e.g., lawn mower and marine engines), additive-ethanol-water phases that form in the distribution system or vehicle fuel tanks will compete with the engine’s lubricating 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, additive-ethanol-water phases will combust in the engine, which may cause damage to the engine. Such damage can occur because the phase is a leaner mixture and will combust at higher temperatures, thereby burning the valve seats.

**Summary:**
Care should be taken to ensure that the ethanol-gasoline blend does not exceed 10 percent ethanol and that water is not allowed to accumulate in the storage and distribution system or in the vehicle fuel system, because engine damage can occur and the vehicle manufacturer warranty would be voided.

**Fuel dispensers**
The September 2000 report by Havill and Associates, EPA Regulated Refueling Facility Market Forecast: 2000-2005, shows that the current dispenser population is over one million. While many dispensers have newer components that may be less affected by alcohol fuels, others may have components that need closer attention. Such components include the following:

- Old Buna-N lathe-cut gaskets and “O” rings. At one time, these were used in about 80 percent of dispensers at about 6 to 30 sealing points inside of each dispenser.
• At one time, old leather meter piston cups were probably used in less than 2 percent of fuel dispensers.

Generally, the failure of the following dispenser component materials that commonly are in contact with the fuel can cause external leakage:

• Aluminum tubing in fuel paths
• Black steel pipe in pipe risers and ground joint unions
• Buna-N in “0” rings and lathe cut gaskets

• Cast iron in meter bodies and fluid paths
• Copper in air eliminator floats
• Hard foamed plastic in air eliminator floats
• Copper tubing in fuel paths
• Cork/Buna-N in flat gaskets
• Die cast aluminum in meter bodies and fluid paths
• Graphite rope in suction pump shaft seals
• Fluorocarbons in “0” rings and lathe cut gaskets

The failure of the following dispenser component materials that commonly are in contact with the fuel can cause malfunction of the storage and distribution equipment:

• Carbon bearings and meter valves
• Cast iron suction pumping units
• Leather meter piston cups (old meters)
• Rulon and graphited Teflon meter piston cups and shaft seals

An example of self-contained pump/dispenser failure occurred in Brazil where automotive fuel often is neat ethanol with approximately 7 percent water content. The pumps are usually suction types using a cast iron internal gear pump that is machined to very close tolerances.

One US pump company ran tests on their cast iron pumping unit by filling it with 93 percent ethanol and 7 percent water and closed the openings with pipe plugs. The pumping unit was opened every month to see if any rust occurred. After testing for over 8 months with no appreciable rust found, several shipments of suction pumps were made to Sao Paulo for installation in service stations.

The pumps lasted less than one week in the Sao Paulo service stations before the cast iron pumping rotors were binding due to rust. When checked, the fuel was 93 percent ethanol and 7 percent water as previously tested. The problem was that the pumps were run until they pumped the underground storage tanks dry. This introduced oxygen into the pumping units and rusting occurred.

**Submersible pumps**

The most common materials exposed to fuel via their use in submersible pumps, the failure of which may cause external leakage, are as follows:

Anodized aluminum pump and motor shells and wiring conduit
Submersible pump materials whose failure can cause a malfunction are as follows:

- Acetal plastic pump impellers and housings
- Black iron fuel piping in the tank
- Carbon motor pump thrust bearings
- Stainless steel motor shells and motor/pump shafts

An example of product failure occurred when winter gasoline with an ethanol oxygenate was introduced to replace non-oxygenated summer gasoline. Although Buna-N lathe-cut gasket seals had been used in the submersible pump flow manifold on top of the tanks for several years, they failed and caused an outbreak of fuel leaks after the introduction of ethanol. However, new Buna-N gaskets do not seem to experience this problem. About 80 percent of the submersible pump manifolds in the field have Buna-N seals, some of which may be the older type.

**Monitoring systems**

Electronic fuel monitoring systems (e.g., tank gauge probes) are relatively new on the scene, having exploded in numbers in the last 10 years. The common materials used for tank gauges in the fuel contact areas are as follows:

- Aluminum electrical conduit
- Epoxy to encapsulate electronic parts
- Glass in capacitance and buoyancy-type probes
- Nitrophyl in magnetostrictive floats
- Nylon for electrical insulation
- PVC jacketed cable for wiring at the top of the probe
- Type 316 stainless steel for magnetostrictive shells

An example of electrolysis corrosion failure of in-tank level gauges was reported early in the 1990s in one tenth of one percent of the probes sold by one manufacturer. These probes used a nylon bushing to prevent electrical contact of the bottom of the probe with the steel tank. Corrosion failure of the probe’s stainless steel shell occurred in as little as 2 weeks.

According to the reports, the culprit was the ethanol oxygenate, which is a slightly conductive polar compound; its use in gasoline permitted an electrical current flow from the stainless steel probe shell around the nylon bushing. The Type 316 stainless steel probe shell was plated away and deposited onto the bottom of the steel tank causing a corrosion failure of the probe. The manufacturer quickly added a nylon coating to the stainless steel probe to a height of 8 inches to prevent a reoccurrence of
Hoses
Materials used in hoses whose failure may cause a fuel leak or a vapor return blockage include the following:

- Epichlorohydrin in the inner fuel-containing walls
- Neoprene in the external cover of the hose
- Nitrile in the inner fluid-containing walls
- Nitrile/PVC in the external cover of the hose
- Nylon used for containing vapor
- Thermoplastics used for containing vapor

Nozzles and Swivels
The most common fuel-immersed materials in nozzles and swivels, the failure of which can cause external leaks, are as follows:

- Buna-N valve poppets and seals
- Die cast aluminum swivel fuel-carrying parts
- Fluorocarbons in valve poppets and seals
- Sand-cast aluminum in fuel-carrying parts
- Super fluorocarbon valve poppets and seals

The most common materials in nozzles and swivels, whose failure can cause an equipment malfunction, are as follows:

- Buna-N valve poppets
- Nickel plating in seal and bearing surfaces
- Stainless steel operating shafts
- Fluorocarbons in valve poppets

In the 1950s through the 1980s, the controlling factor in seal material selection was which material could cost effectively meet UL listing requirements.

At that time, fluorocarbon parts cost 10 times more than Buna-N. Therefore, Buna-N was chosen nearly 100 percent of the time. Buna-N would not be the preferred choice for ethanol fuels. The Havill report indicates that nozzle and swivel life span is approximately 17 to 24 months, respectively.

Thus, UL listed components should contain ethanol-gasoline resistant seal materials. However, it has been estimated that a nozzle body is refurbished up to eight times before it is discarded. This refurbishing of nozzles and swivels by field personnel may not include alcohol fuel resistant materials. Such components should be monitored for potential failure.
Piping
The September 2000 Havill study reported that, at the time of the mid-year survey, the most common material in use for underground flammable and combustible piping was thermoset rigid fiberglass (55 percent) followed by thermoplastic flexible (36 percent), cathodically protected steel (7 percent) and “other,” including copper (2 percent). Thus, 91 percent of the installed underground piping is non-metallic. However, nonmetallic piping differs in that thermosetting resins reinforced with fiberglass (i. e., fiberglass rigid piping) are cured into an irreversible matrix, whereas thermoplastic resins (i. e., thermoplastic flexible piping) are a semi-crystalline or a glassy amorphous material that is reversible.

Fiberglass rigid piping.
In 1968, Underwriters Laboratories first listed nonmetallic piping for flammable and combustible liquid service. At that time the UL 971 Nonmetallic Underground Piping for Flammable Liquids test protocol stated that “there shall be no loss of weight in any of the test samples” (i. e., no permeability) over the test period. However, it was not until 1984 that the UL 971 protocol included compatibility and permeability testing with various percentages of ethanol in gasoline blends up to and including 100 percent ethanol.

The 1999 Shell Oil paper reported that “Smith Fiberglass attempted to measure permeation of EtOH in fiberglass piping after 31 days exposure and they were unable to find any.” On May 24, 2000, Smith Fiberglass advised the EPA that UL-Listed RED THREAD pipe was listed in 1968 for petroleum products only. However, the letter also states that, since that time, “Smith Fiberglass Products Inc. recommended this pipe for methanol/gasoline blends up to 5 percent methanol at temperatures up to 75° F. The pipe was also recommended for all mixtures of ethanol and gasoline including 100 percent ethanol.”

Thermoplastic flexible piping.
In 1995, Underwriters Laboratories established the UL 971 standard for permeability testing of nonmetallic piping to permit a permeation leak rate. The permissible permeation rate was up to 0.013 oz/sq. ft./day for the primary pipe and 0.079 oz/sq. ft./day for the secondary containment piping. Thus, the revised UL 971 permits a permeability leakage of:

• 0.16 gallons per 100 feet in 30 days in a 2-inch I.D. primary pipe and
• 1.0+ gallons per 200 feet in 30 days in a +2-inch I.D. secondary pipe.

A paper distributed at the 1998 Petroleum Equipment Institute annual trade exhibition states that “both the materials and the construction of each pipe vary significantly from manufacturer to manufacturer.” This includes nylon “used by some manufacturers as a primary pipe liner material. This, in fact, was the norm before the introduction of alcohol fuels. Nylon, however, provides only a marginal permeation barrier in the presence of ethanol and methanol.”

The 1999 Shell Oil paper reported “In general, fluorinated elastomers and thermoplastics offer better permeation resistance than non-fluorinated materials.” And, the UL listing of nonmetallic piping for
flammable and combustible liquids includes a 180-day permeability test that includes ethanol. However, while fiberglass piping was listed to meet the pre-1995 allowable permeation rate, flexible pipe permeation rates are proprietary.

**Tanks**

The September 2000 Havill study reports that, at the time of the mid-year survey, there were over 700,000 regulated petroleum underground storage tanks. Of this total, 60 percent were fiberglass and 28 percent were sti-P3 steel tanks with external cathodic protection.

**Fiberglass tanks.**

The 1999 Shell Oil paper reports that polyester matrix composites are used in nonmetallic underground storage tanks. This was also the composite used before 1978, when the federal National Energy Act and certain states initiated tax relief incentives for ethanol-gasoline blends. The incentives increased the use of ethanol as a gasoline component “significantly,” according to API. As a result, API member companies, recognizing that the introduction of gasohol fuels in existing storage and handling systems required special handling, developed API RP1626, Storing and Handling Ethanol and Gasoline-Ethanol Blends at Distribution Terminals and Service Stations.

In addition, fiberglass tank manufacturers worked with resin manufacturers and confirmed that the “polyester matrix composites” used were compatible with gasohol fuels. Consequently, in 1981 the two major fiberglass tank manufacturers added gasohol fuels to their warranty for current tanks that continued to be manufactured with the same polyester matrix composites. Later, in 1989, Amoco Chemical Company reported on long term compatibility testing of isopolyester resin underground storage tank samples in gasohol (and other fuel components, including methanol) and found no significant resin deterioration.

To address the subject of alcohol-gasoline compatibility stored in pre-1981 and post-1981 fiberglass tanks, Owens Corning wrote a letter dated May 8, 2000. This letter states that, while Owens Corning did not identify 10 percent alcohol as a fuel earlier, “Owens Corning knows of no technical reason why properly installed pre-1981 tanks should not perform equally as well as post-1981 tanks when used to store fuels containing 10 percent ethanol.”

Beginning in 1982, the UL #1316 test protocol was expanded to include immersion and physical testing of fiberglass tank samples in higher concentrations of ethanol-gasoline test liquids. Consequently, single wall tanks may be UL listed for alcohol fuels (e.g., 100 percent ethanol, 100 percent methanol, and 85 percent ethanol), and double wall fiberglass tanks are listed for all fuels, including alcohols. The UL listing label is affixed to the fiberglass tank exterior adjacent to a lifting lug and identified on the tank invoice. However, if this information is unavailable, tank manufacturers maintain a library of UL listing specifications (including, for example, the listing for product service, capacity, model, and shipping date) based on the shipped-to address. Thus, a purchaser of an existing UST facility may determine tank information from the manufacturer.
Steel Tanks.
The 1999 Shell paper addressed what was termed “wet corrosion” that occurs in the low aqueous phase (see above for a discussion on ethanol-gasoline blends and water). “The aqueous phase becomes saturated with alcohol and ionic contaminants.... In the lower aqueous phase, reactions involving oxygen are more pronounced because the solubility of oxygen is greater in the aqueous phase than in the hydrocarbon phase....Ionic species increase the conductivity of the media, thereby speeding the electrochemical process at the anode and the cathode.”

A 1999 Modern Welding Company installation and warranty publication states, “The primary tank should be inspected monthly for the presence of water. Water and sediment in fuel can cause plugging of filters. Also, bacterial growth originating from the fuel can cause filters to plug and tanks and lines to corrode. Failure to remove water from the tank may void your warranty.”

Tank water bottoms
It is clear from the foregoing that ethanol-gasoline blends should be controlled to not exceed 10 percent ethanol in the blend and that water bottoms should be avoided. Otherwise, the following could occur:

• Vehicles could be damaged
• Fuel dispensing components could be damaged
• Allowable permeation rates could be exceeded
• Tank life could be jeopardized

API member companies addressed the need to control the ethanol blend component in the 1985 API RP1626, which states: “In-truck blending is not recommended since complete blending may not occur.” Also, API RP1626 (1985), RP1627 (1986) and RP4261 (1988) all recommended tank water bottom removal when storing alcohol-gasoline fuels.

Conclusion
Those considering ethanol fuels as an alternative to MTBE should also consider protecting the motoring public’s vehicles from damage and the environment from discharges caused by equipment damage.

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