



Motor Gasolines

Technical Review



4 • Oxygenated Gasoline

Oxygenated gasoline is not new; oxygenates have been added to gasoline for decades. Prior to 2006, methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME) along with smaller quantities of ethyl tertiary butyl ether (ETBE) were used in U.S. gasoline. Today, ethanol, also called *ethyl alcohol* or *grain alcohol*, is used almost exclusively.

Widespread use of ethanol in the United States began in 1978 when a Nebraska group marketed gasoline containing 10 volume percent ethanol as *gasohol*. The program was intended to help increase gasoline availability during the energy crisis of that decade. Later, the *gasohol* name was abandoned, but the use of ethanol continued. Much of the early ethanol-blended product was marketed in the Midwestern states, where the bulk of ethanol is produced.

In the 1990s, air quality regulations required gasolines in some parts of the United States to be oxygenated either in the winter or else year-round. (See page 27 for information regarding gasolines in carbon monoxide [CO] nonattainment areas and Federal Phase I and California Phase 2 reformulated gasolines [RFG].) By 2001, about 10 percent of all the gasoline sold in the U.S. contained ethanol and 58 percent of the blends contained 10 volume percent ethanol, often referred to as *E10*. Initially, little RFG contained ethanol.

As noted in Chapter 3, “Gasoline Refining and Testing,” MTBE was used as an oxygenate to meet U.S. Environmental Protection Agency (EPA) and California Air Resources Board (CARB) reformulation requirements. The first U.S. EPA waiver for MTBE use was issued in 1979 for 7.0 volume percent, and a second waiver for 15.0 volume percent was issued in 1988. MTBE was not widely used until the late 1980s, and then its use expanded with the introduction of federal RFG in 1995. California banned the use of MTBE and other ethers and heavy alcohols as of January 1, 2004. A number of other states followed California’s lead, which greatly diminished MTBE use. In 2006, the U.S. EPA rescinded the oxygenated gasoline requirement in federal RFG, as required by the Energy Policy Act of 2005. This resulted in the removal of virtually all MTBE from the U.S. gasoline pool. Gasoline refiners in the U.S. ceased using MTBE, and by default, ethanol became the oxygenate component used almost exclusively.

CHEMISTRY

Oxygenated gasoline is a mixture of conventional hydrocarbon-based gasoline and one or more oxygenates. Oxygenates are combustible liquids made up of carbon, hydrogen, and oxygen. All the oxygenates currently used in gasoline belong to one of two classes of organic molecules: alcohols and ethers.¹ In alcohols, a hydrocarbon group and a hydrogen atom are bonded to an oxygen atom: R-O-H, where *R* represents the hydro-

¹ The word *ether* reminds many people of the anesthetic. Although the anesthetic commonly is called ether, its chemical name is diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$). It is not used as a gasoline oxygenate because it is too volatile.

Table 4.1

Oxygenates for Gasoline

Name	Formula	Structure	Oxygen Content Mass %	Blending Research Octane Number (BRON) ¹	Maximum Concentration Approved by EPA ²	
					Mass % Oxygen	Volume % Oxygenate
Ethanol (EtOH)	C ₂ H ₆ O	CH ₃ -CH ₂ -OH	34.73	129	(3.70) ³	10.0 ⁴
Methyl Tertiary Butyl Ether (MTBE)	C ₅ H ₁₂ O	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{O}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} $	18.15	118	(2.74)	15.0
Ethyl Tertiary Butyl Ether (ETBE)	C ₆ H ₁₄ O	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}_2-\text{O}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} $	15.66	119	2.70	(17.3)
Tertiary Amyl Methyl Ether (TAME)	C ₆ H ₁₄ O	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{O}-\text{C}-\text{CH}_2-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} $	15.66	119	2.70	(16.6)

¹ RON of the pure compound that is consistent with the RON of the oxygenate-gasoline mixture obtained by blending.

² Values in parentheses are approximations calculated from the regulated limit using the known specific gravity (relative density) of the oxygenate and a typical relative density of gasoline of 0.74.

³ Assuming pure, undenatured ethanol. For denatured ethanol the value would be slightly lower.

⁴ EPA limit is 10.0 vol % denatured ethanol. Denatured ethanol may have a purity of 92.0 vol % to 98.0 vol %.

carbon group. All alcohols contain the OH atom pair. In ethers, two hydrocarbon groups are bonded to an oxygen atom; the groups may be the same or different: R-O-R or R-O-R' (the apostrophe is used to indicate a different hydrocarbon group).

USE

The U.S. EPA regulates which oxygenates and in what concentrations they can be added to gasoline in the U.S. through the Substantially Similar Rule and waivers (see sidebar on page 57). Table 4.1 summarizes such information. Note that, on a volume basis, each ether has a different maximum concentration because each has a different oxygen content and relative density.

Table 4.2 provides the ranges of oxygenate use – in terms of oxygen content of the gasoline – required by U.S. federal and California regulations. Any oxygenate use conforming with the U.S. EPA's Substantially Similar or waiver conditions is acceptable federally, but many states are in the process of banning or have banned the use of MTBE. Some states have banned the use of all ethers and heavy alcohols. The use of ethanol is encouraged by the U.S. Renewable Fuel Standard.

Usually, ethanol is blended with gasoline at terminals in the tank trucks that will deliver the blends to service stations. Terminal blending involves more operating and capital expense than refinery blending, but it avoids the product integrity concerns associated with bulk transport of gasoline-ethanol blends (discussed later). However, because ethanol can raise octane and volatility of blends, it typically needs to be blended with a lower-octane, reduced-volatility conventional gasoline to help ensure the final gasoline-ethanol blend meets finished fuel specifications and regulations. In the case of RFG, this base fuel is called reformulated blendstock for oxygenate blending, referred to as *RBOB*. In California, it is called *CARBOB*.

Table 4.2

Oxygen Content Required by U.S. Emissions Regulations

Regulation	Oxygen Content, Mass Percent	
	Minimum	Maximum ¹
CO Nonattainment Areas² (4 or 5 winter months)		
California	1.8	2.2
Other States	2.7	3.7 ³
Federal RFG^{4,5}		
Complex Model		
Phase II	0	4.0 ⁶
California Phase 3 RFG²		
Summer		
Flat Limit	1.8	2.2
Predictive Model	0	3.5 ⁸
Winter		
Flat Limit	1.8	2.2
Predictive Model	1.8 ⁷	3.5 ⁸

¹ Regardless of this limit, specific oxygenates may not exceed their Substantially Similar or waiver limits. For example, the Substantially Similar maximum limit for ethers such as MTBE is 2.7 mass % oxygen (2.9 mass % in CO nonattainment areas in the winter).

² Per gallon limits.

³ The maximum winter limit for Substantially Similar oxygenates is 2.9 mass % in CO nonattainment areas.

⁴ Average limits.

⁵ CO nonattainment area oxygen limits take precedence over RFG oxygen limits in CO nonattainment areas in the winter.

⁶ Upper limit of valid range for oxygen content variable in model.

⁷ The minimum limit only applies during specified winter months in specified CO nonattainment areas.

⁸ If the gasoline contains more than 3.5 mass % oxygen but no more than 10 vol % ethanol, the maximum oxygen content cap is 3.7 mass % oxygen.

Methanol Is Not Ethanol

Ethanol and methanol should not be confused; they are different compounds. While gasoline oxygenated with methanol and its cosolvents has been available in limited amounts, its use is currently prohibited. Major differences between the two compounds include:

- Gasoline oxygenated with methanol corrodes fuel system metals and accelerates deterioration of elastomers.
- Gasoline oxygenated with methanol is not approved for use by many vehicle manufacturers.
- Adding methanol to gasoline significantly increases the vapor pressure of the blend – an undesirable effect in this era of more stringent volatility controls.
- Methanol, unlike ethanol, is toxic.

Table 4.3

EN 228: Oxygenates Requirements

Oxygenate	Maximum Vol %
Methanol	3
Ethanol	5
Isopropyl Alcohol	10
Isobutyl Alcohol	10
Tert-Butyl Alcohol	7
Ether (5 or more C atoms)	15
Other Oxygenates	10

As long as U.S. EPA concentration limits are observed, oxygenates may be used in areas of the U.S. where adding oxygenates is not required to meet wintertime CO nonattainment requirements. This is allowed when the octane of the gasoline needs enhancement and when adding oxygenates is more cost-effective than other methods. Further, renewable oxygenates must be used to comply with the U.S. Renewable Fuels Standard and EU Biofuels Directive.

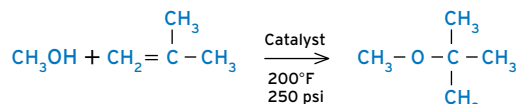
The information available to retail consumers about the oxygenate composition of gasoline varies. Labeling is controlled by state, not federal, regulations. Some states require dispenser labels for oxygenated gasolines in wintertime CO nonattainment areas and for RFG. A typical label reads: *The gasoline dispensed from this pump is oxygenated and will reduce carbon monoxide pollution from motor vehicles.* Such labels do not provide any information about which oxygenate(s) the blend contains; others do. The National Conference on Weights and Measures (NCWM), an association of state weights-and-measures agencies responsible for dispenser calibration and labeling, issued a revised standard guideline for dispenser labeling in 1996. Some states follow the NCWM guidelines, some follow modified versions, and others have their own requirements.

In Europe, the EN 228 specification limits the maximum amounts of various oxygenates in gasoline (see Table 4.3). The European Union has set targets for each member state for the market share of biofuels. These targets are based on the challenging benchmarks set by Directive 2003/30/EC: 2 percent market share by December 2005 and 5.75 percent market share by December 2010.

In Japan, JIS K 2202 allows MTBE only up to 7 volume percent. Canada limits methanol to 0.3 volume percent, other oxygenates to 2.7 mass percent oxygen, and ethanol specifically to 10 volume percent maximum. In Brazil, Agência Nacional do Petróleo (ANP) Regulation No. 309 stipulates that only Type C gasoline may be sold. The ethanol content and specifications are set by separate legislation, and the current required ethanol content is 25 volume percent (plus or minus 1 percent). Conventional vehicles in Brazil are calibrated to use this high level.

SOURCES

Ethanol can be synthesized from petroleum by hydrating ethylene, but most of it (94 percent of the worldwide supply in 1993) is derived from the fermentation of carbohydrates, principally corn in the United States. Sugar cane is used in many parts of the world. The process involves distillation to separate ethanol from fermentation residues, dehydration to remove the water that co-distills with the alcohol, and, for fuel ethanol, addition of a noxious or toxic material (denaturing) to make it unfit for human consumption.



MTBE is derived from methanol and isobutylene. A catalyst is used to assist the reaction.

Most methanol is produced from natural gas (methane). Isobutylene is obtained from petroleum, either as a byproduct of the refining process or from butane. Although it is made from methanol, MTBE is a different material with different properties. For instance, MTBE doesn't have methanol's corrosivity and toxicity defects (see sidebar on page 55).

The other ethers are made by similar processes. ETBE is derived from ethanol and isobutylene. TAME is derived from methanol and isoamylenes.

SPECIFICATIONS

ASTM D4806 *Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel* is used to specify product quality for ethanol in the United States. CARB specifies D4806 with additional content limits on sulfur, aromatics, benzene, and olefins for California Phase 3 RFG. D4806 limits denaturants to hydrocarbons boiling in the gasoline range because of harmful side effect concerns for other materials.

ASTM D5983 *Standard Specification for Methyl Tertiary-Butyl Ether (MTBE) for Downstream Blending for Use in Automotive Spark-Ignition Engine Fuel* is used for merchant MTBE in the United States.

PERFORMANCE ISSUES

Fuel Leaning Oxygenated gasoline leans the air-fuel mixture of carbureted engines and fuel-injected engines that have older open-loop fuel systems. If an open-loop fuel system is set to provide a very fuel-rich mixture, fuel leaning might help improve performance. Otherwise, fuel leaning can degrade driveability; the extent depends on an engine's calibration.

Newer engines have closed-loop air-fuel ratio control incorporating an electronic control module (ECM, see page 69) that adjusts air-fuel ratio to compensate for oxygen in fuel. However, an ECM may default to preset open-loop calibrations when an engine is cold and its oxygen sensor is not at operating temperature, when power demand is high (such as during rapid acceleration), or when the exhaust oxygen sensor is defective. Under such conditions, oxygenated gasoline leans the air-fuel mixture in newer engines like it does in older open-loop fuel systems. Vehicles with adaptive learning can compensate for changes in stoichiometric air-fuel ratio.

Ethanol has a higher heat of vaporization than ethers. Some of the degradation in driveability experienced with gasoline oxygenated with ethanol can be attributed to the additional heat needed to vaporize the fuel.

Volatility Adding ethanol to a conventional gasoline not designed for alcohol blending can produce a blend that exceeds RFG vapor pressure limits. In conventional gasoline that has a vapor pressure of 62 kPa (9.0 psi), ethanol can raise vapor pressure 6.9 kPa (1.0 psi);

U.S. Oxygenate Regulation and the Substantially Similar Rule

The Clean Air Act Amendments of 1977 control the use of oxygenates in unleaded gasoline. The purpose of the amendments is to ensure that oxygenate use won't contribute to emission control system failures that could result in increased emissions. The regulations that the U.S. EPA developed to implement the law prohibit the introduction or increase in concentration of a fuel or fuel additive that is not substantially similar to any fuel or fuel additive used in the certification of any 1975 or subsequent model-year vehicle.

In 1981, the U.S. EPA issued the Substantially Similar Rule, recognizing that the use of certain types of oxygenates was safe below a specified oxygen content. The rule, as revised in 1991, allows aliphatic alcohols (excluding methanol) and/or aliphatic ethers to be blended into gasoline up to a concentration that would result in 2.7 mass percent oxygen in the blend. The rule requires the finished blend to possess all the physical and chemical characteristics of an unleaded gasoline specified by ASTM D4814-88 for at least one of the seasonal and geographic volatility classes.

U.S. EPA regulations also created a process by which a waiver could be granted for an oxygenate recipe that an applicant has demonstrated will not cause or contribute to the failure of any emission control device or system. The U.S. EPA has granted waivers for concentrations of ethanol in gasoline up to 10 volume percent. (The mass percent

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oxygen content of this blend depends on the density of the gasoline. For gasoline with the typical relative density of 0.74 at 15.6°C [60°F] blended with 10 volume percent pure ethanol, the resulting oxygen content is 3.7 mass percent. For the same gasoline blended with 10 volume percent denatured ethanol, the resulting oxygen content is 3.5 mass percent). The U.S. EPA also has ruled that gasolines containing up to 2.0 volume percent MTBE (not purposely added) that are subsequently blended with 10 volume percent ethanol (resulting in a total oxygen content of 4.0 mass percent if blended with pure ethanol) do not violate the ethanol waiver. This ruling was made to assure an adequate supply of base gasoline for blending with ethanol.

The U.S. EPA also has granted waivers for blends of gasoline and gasoline-grade tertiary butyl alcohol (TBA) up to 3.5 mass percent oxygen content (16 volume percent TBA) and for various blends of methanol and gasoline-grade TBA or other higher-molecular-weight alcohols (cosolvents).

Further, any fuel or fuel additive registered with the U.S. EPA must have a supplemental registration involving toxicity that may require additional toxicity testing. None of the methanol-containing waivers has a supplemental registration. Oxygenates that were not initially registered now will require full toxics studies to be completed before they can be used.

in RBOB that has a vapor pressure of 39.6 kPa (5.7 psi), ethanol can raise vapor pressure 9.0 kPa (1.3 psi). This increase, coupled with the corresponding reduction in mid-range distillation properties, lowers the V/L = 20 temperature, reducing vapor lock protection. Blend volatility is increased only slightly by MTBE and not at all by ETBE and TAME.

Because it significantly increases fuel volatility, ethanol has not been the oxygenate of choice for summer RFGs, which have very tight vapor pressure limits. Now, with increasing use of ethanol, hydrocarbons with higher volatility must be removed during the production of RBOB to help ensure the final gasoline-ethanol blend meets specifications and complies with regulations.

Commingleing, another volatility issue, can occur if ethanol-blended fuel is mixed with hydrocarbon-only fuel in a vehicle fuel tank. In effect, the ethanol in the ethanol blend increases the vapor pressure of the hydrocarbon-only gasoline. The increase in vapor pressure is dependent on the ratio of the two components and the amount of ethanol in the blend. The maximum effect of about 6.2 kPa (0.9 psi) increase occurs for a 5.7 volume percent ethanol blend when the mixture contains about 75 percent hydrocarbon-only gasoline where both fuels initially have a vapor pressure of 48.3 kPa (7.0 psi).

Water Tolerance Conventional gasoline, depending on its aromatics content, can dissolve up to 150 parts per million (ppm) water at 21°C (70°F). Oxygenating gasoline with ethers can increase water solubility to 600 ppm. Contacting either conventional gasoline or ether-oxygenated gasoline with additional water will not affect the properties of the gasoline but can make it appear hazy.

Water-saturated blends become hazy when cooled because some of the water becomes insoluble. However, the water that is released does not contain much ether, and the blends do not contain enough water to cause performance problems.

The situation is different for gasoline oxygenated with 10 volume percent ethanol. The gasoline-alcohol blend can dissolve more water (6,000 ppm to 7,000 ppm at 21°C/70°F). When this blend is cooled, both the water and some of the ethanol become insoluble. Contacting the blend with more water also draws ethanol from the blend. The result, in both cases, is two layers of liquid: an upper ethanol-deficient gasoline layer and a lower ethanol-rich water layer. Depending on how much water is present, up to 90 volume percent of the ethanol in the gasoline phase can be extracted into the water phase. This process, called *phase separation*, occurs because ethanol is completely soluble in water but only marginally soluble in hydrocarbons. After phase separation, the gasoline layer will have a lower octane number and may cause knocking. The fuel also is less volatile. An engine will not run on the water-ethanol layer. As the concentration of ethanol is decreased, or as the aromatics content of the gasoline is decreased, or as temperature is decreased, less water is required to cause a phase separation.

Because of the potential for phase separation, gasoline-ethanol blends should not be exposed to water during distribution or use in a vehicle. Consequently, gasoline-ethanol blends are not transported in pipelines, where water may accumulate in low spots. Rather, ethanol is added to tanker trucks at a terminal immediately before delivery to service stations. Good housekeeping at a service station is also very important to help prevent water contamination. This sensitivity to water also means that extra care should be taken when gasoline-ethanol blends are used as a fuel for boat engines. Gasoline-ethanol blends are hygroscopic (absorb moisture from the air). During long-term storage, gasoline-ethanol blends can phase-separate if a storage tank is vented to the atmosphere and subject to breathing as a result of temperature changes.

Material Compatibility Some fuel system metal components will rust or corrode in the presence of water or acidic compounds. The additional water dissolved in oxygenated gasolines does not cause rusting or corrosion, but water resulting from phase separation of gasoline-ethanol blends will, given time.

Oxygenates can swell and soften natural and some synthetic rubbers (elastomers). Oxygenated gasolines affect elastomers less than oxygenates do, the extent of which depends on the type of elastomer and on the hydrocarbon chemistry of the gasoline, particularly its aromatics content. The effect is of potential concern because fuel systems contain several types of elastomers in hoses, connectors (O-rings), valves, and diaphragms. The elastomeric materials used in today's vehicles in the U.S. have been selected to be compatible with oxygenated gasolines. In their owner's manuals, vehicle and equipment manufacturers typically indicate whether the use of oxygenated gasolines is acceptable. Manufacturers approve the use of gasoline oxygenated with up to 10 volume percent ethanol or 15 volume percent MTBE. (The compatibility of other ethers is the same as that of MTBE.) The approved levels may be higher or lower outside the United States.

Automobile and equipment manufacturers upgraded their fuel system elastomers at different times. Elastomers in U.S. vehicles manufactured before 1975 may be sensitive to oxygenated and high-aromatics gasolines. In U.S. vehicles manufactured between 1975 and 1980, elastomers were upgraded but not to the same extent as later models.² Elastomer compatibility in other parts of the world may not be the same as in the United States.

Recent claims contend that certain older fiberglass fuel tanks contain resins that are incompatible with ethanol. Such tanks had been used at one time for bulk gasoline storage, and they may be found in certain older boats. Owners of older boats or boats that include older fuel storage systems should consult the manufacturer to determine compatibility.

² Reynolds, Robert E., et al., *Changes in Gasoline III*, Downstream Alternatives, Inc., Bremen, Ind., 1996.

Chevron has not observed a significant compatibility problem between oxygenated gasolines and elastomers in older U.S. cars. There was not an increase in problems when oxygenated gasoline was introduced in 39 metropolitan areas in the winter of 1992. This held true for the Western states, which tended to have a higher number of older cars in their vehicle populations, and for areas where different oxygenates were used (MTBE, and now ethanol throughout California and in Portland, Oregon, and Seattle/Tacoma, Washington).

Fuel Economy The effect of oxygenated gasoline on fuel economy is discussed on page 9.

Permeability Gasoline components diffuse through elastomeric hoses and seals and through plastic fuel tank surfaces and contribute to evaporative emissions. Compared to non-ethanol gasolines, gasolines that contain ethanol worsen the problem in two ways: not only does ethanol permeate non-metal fuel system components, but a larger amount of gasoline hydrocarbons do, too. Studies conducted by the Coordinating Research Council³ show that permeation emissions through vehicle fuel system elastomers increase on average by about 65 percent for a typical California Phase 3 gasoline oxygenated with 5.7 volume percent ethanol compared to a typical California Phase 2 gasoline oxygenated with 11 volume percent MTBE or to a non-oxygenated Phase 3 gasoline.

³ *Fuel Permeation from Automotive Systems*, No. E-65, Coordinating Research Council, Alpharetta, Ga., September 2004; and *Fuel Permeation from Automotive Systems: E0, E6, E10, E20 and E85*, No. E-65-3, Coordinating Research Council, Alpharetta, Ga., December 2006.