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National Renewable Energy Laboratory*

**NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.**

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## List of Acronyms and Abbreviations

°C	degrees Celsius
°F	degrees Fahrenheit
ABE	ABE fermentation (so called because it produced acetone, butanol, and ethanol)
AKI	anti-knock index
AMF	acetoxymethyl furfural
API	American Petroleum Institute
ASTM	ASTM International
BL	butyl levulinic acid
Btu	British thermal unit
CFR	Code of Federal Regulations
CO	carbon monoxide
CRC	Coordinating Research Council
DI	driveability index
DMF	dimethylfuran
EL	ethyl levulinic acid
EMF	ethoxymethyl furfural
EP	ethyl pentanoate
EPA	U.S. Environmental Protection Agency
FFV	flex fuel vehicle
FR	Federal Register
g	gram
gal	gallon
GHB	$\gamma$ -hydroxybutyrate
GTBA	gasoline-grade t-butyl alcohol
GVL	$\gamma$ -valeralactone
H <sub>2</sub>	hydrogen
HC	hydrocarbons
HMF	hydroxymethyl furfural
IARC	International Agency for Research on Cancer
J	joule
kcal	kilocalorie
kg	kilogram
kPa	kilopascal
L	liter
LA	levulinic acid
lb	pound
MF	2-methylfuran
mg	milligram
MJ	megajoules
mL	milliliter
MON	motor octane number
MP	methyl pentanoate
MTHF	2-methyltetrahydrofuran
NIST	National Institute of Standards and Technology

NMOG	non-methane organic gases
NO <sub>x</sub>	nitrogen oxides
NREL	National Renewable Energy Laboratory
PA	pentanoic acid
ppm	part per million
psi	pounds per square inch
RFG	reformulated gasoline
RON	research octane number
RVP	Reid vapor pressure
UL	Underwriters Laboratories
vol%	percent volume
wt%	weight percent

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## EXECUTIVE SUMMARY

This report reviews the use of higher alcohols and several cellulose-derived oxygenates that, as blend components in gasoline, can reduce our dependence on petroleum-derived fuel. Higher alcohols (with the exception of tert-butanol) can be produced from sugars via fermentation or by gasification to form synthesis gas, followed by catalytic conversion to a mixture of alcohols. Five-carbon alcohols can also be produced from sugars or ligno-cellulosic biomass by chemical means. Levulinic acid esters (ethyl and butyl), methyl pentanoate (MP),  $\gamma$ -valerolactone (GVL), methyltetrahydrofuran (MTHF), 2-methylfuran (MF), and dimethylfuran (DMF) can also be produced by chemical transformation of ligno-cellulosic biomass and have been proposed as gasoline extenders.

While data on the use of these compounds as fuel components are limited, there is evidence that some may provide benefits such as higher energy density, lower vapor pressure, lower affinity for water, and potentially improved material compatibility relative to first generation biofuels. None of these oxygenates can be used neat in the existing U.S. auto fleet because the vapor pressure of each of these materials alone is too low to allow reliable startup. Like fuel-grade ethanol, however, neat higher alcohols up to C<sub>4</sub>, as well as DMF, MF, and MP, have a vapor composition in the flammable range at normal ambient temperatures and so must be handled appropriately at production facilities and blending terminals. Material compatibility issues are expected to be less severe for neat higher alcohols than for fuel-grade ethanol. There is limited information regarding materials compatibility of the other oxygenates.

In contrast to gasoline, alcohols up to C<sub>4</sub> will take up (dissolve) significant amounts of water. Ethanol, methanol, tert-butanol, and GVL are completely miscible with water; the other alcohols and oxygenates less so. However, most of these compounds when dissolved in gasoline and in contact with sufficient quantities of water will form two phases. The aqueous phase may contain significant quantities of oxygenate, reducing the oxygenate content of the gasoline and potentially causing the gasoline phase to fail ASTM specification requirements and give unacceptable performance. Thus, for these oxygenates, exposure to water will still need to be controlled, although the impact of water exposure will be less than it would be for fuel-grade ethanol.

To limit impurities and constrain other fuel properties, it is likely that an ASTM standard for blend components, similar to ASTM D4806 for fuel-grade ethanol, will need to be developed prior to introduction of these components into the commercial fuel supply. Development of an ASTM specification will require a substantial amount of data on the chemical composition and properties of the oxygenate of interest as well as on how the main component and impurities impact the durability of the engine and emission control system. At this time, little is known about the potential for by-products and minor contaminants that may be present in these oxygenates from the various production processes, a data gap that will need to be addressed.

Very little data exist on how blending higher alcohols or other oxygenates with gasoline or unfinished gasoline (blendstock for oxygenate blending) affects the D4814 properties. Furthermore, the Driveability Index, one of the properties of D4814, is not defined for oxygenates other than ethanol.

Under the Clean Air Act, fuels used in the United States must be “substantially similar” to fuels used in certification of cars for emission compliance. This is generally interpreted as meaning that fuels must be substantially similar to gasoline. Aliphatic ethers and alcohols, which include MTHF and all of the higher alcohols but not the other oxygenates in this report, and their mixtures at concentrations up to 2.7 wt% oxygen were made substantially similar by rule. Waivers for the addition of higher alcohols at concentrations up to 3.7 wt% oxygen have also been granted. DMF and MF (aromatic compounds) and the ester oxygenates are not substantially similar and will require a large body of test data to show that they do not “cause or contribute” to the failure or deterioration of any emission control device to obtain a waiver. Furthermore, the Clean Air Act requires that fuels be registered with the U.S. Environmental Protection Agency, which requires the submission of basic data on the composition and health impacts of the fuel. The fuel registration requirements have not been completed for any of the oxygenates discussed in this report, although the process is underway for isobutanol.

Limited emission testing performed on pre-Tier 1 vehicles and research engines suggests that higher alcohols will reduce emissions of carbon monoxide and organics, while nitrogen oxide emissions will stay the same or increase. It is not clear that these effects would be observed in modern Tier 2 vehicles. In addition, there is no publicly available information on the impact of these oxygenates on emissions of specific toxic compounds. The impact of these oxygenates on evaporative emissions, including permeation effects, has not been studied, nor has the impact on the durability of emission control catalysts.

Based on the available evidence, the properties of MTHF, DMF, MF, and MP suggest that they may function well as low-concentration blends with gasoline in standard vehicles and in higher concentrations in flex fuel vehicles. The high toxicity of DMF and MF warrants special care in assessing emissions and the potential for environmental damage to ensure their use would not present an exceptional risk. Safety issues associated with the formation of peroxides in MTHF will also need to be assessed.

Fuel use of GVL will be held back by its potential for abuse as a drug. Although ethanol also has the potential for abuse and addiction, its widespread availability elsewhere minimizes the potential for additional disruption caused by fuel use. In addition, GVL’s miscibility with water and its high boiling point (and presumably low vapor pressure at typical ambient temperatures) present significant drawbacks to its use as a gasoline substitute or additive. Similarly, the miscibility of tert-butanol with water will likely limit its use.

The volatility of low-concentration levulinate/gasoline blends should be measured. However, based on the limited information available on boiling points, there is some evidence that the levulinate compounds may not be volatile enough to be used in existing vehicles.

Testing to obtain the approval of Underwriters Laboratories (or another nationally recognized testing laboratory) for the use of dispensers and aboveground and underground storage tanks with higher alcohols and other oxygenates will be required for widespread commercialization.

In the longer term, investigations are needed into the performance of these oxygenates in advanced engines employing direct injection or low-temperature combustion strategies.

# 1 INTRODUCTION

Gasoline has been used to fuel spark-ignition vehicles for over 100 years. Over time, the vehicles themselves have been adapted and optimized to run on gasoline, and a complex infrastructure to store and distribute the fuel has been developed. Although gasoline is by far the predominant fuel for spark-ignition vehicles, various alcohols have been used in cars from the time of the first Model T, which was originally designed to run on ethanol or gasoline. Methanol has a long history as a racing fuel. Ethanol is used extensively as a blend component at up to 10 volume percent (vol%) in gasoline, and in 2010 over 13 billion gallons of were used.<sup>1</sup> Ethanol is also used to reduce emissions of carbon monoxide and other pollutants. At concentrations as high as 85% in gasoline, ethanol can be used in flex-fuel vehicles (FFVs). The higher alcohols (with three or more carbons) could provide significant advantages over ethanol, most notably their higher energy density, lesser effect on gasoline/blend vapor pressure, lower affinity for water, and improved material compatibility. Higher alcohols or blends of higher alcohols can also be produced from ligno-cellulosic biomass, resulting in additional petroleum displacement.

More recently, scientists have proposed several other compounds synthesized from renewable sources as potential fuels. These compounds may be less expensive to produce or have characteristics that address some of the drawbacks of ethanol. Most importantly, they are produced from cellulosic biomass, the largest potential resource for biofuel production.<sup>2</sup> The compounds reviewed here include 2-methyl tetrahydrofuran (MTHF), dimethylfuran (DMF), methylfuran, (MF),  $\gamma$ -valerolactone (GVL), levulinic acid esters [ethyl (EL) and butyl (BL)], and methyl pentanoate (MP). Like ethanol, all of these compounds can be produced from sugars or from ligno-cellulosic biomass. All have been proposed in the scientific literature, by patent holders, or by potential manufacturers as gasoline biofuels.

Numerous issues will need to be addressed before these new fuel blend components can be fully accepted commercially:

**How will different concentrations fit into the existing regulatory framework for spark-ignition fuels?** The U.S. Environmental Protection Agency (EPA) already permits aliphatic alcohols and ethers to be added to gasoline in limited concentrations. However, esters and aromatic furanics are not currently permitted. The applicable regulations and waivers are reviewed in Section 4.1.

**How well will the new oxygenates work in existing engines?** The ASTM standard for automotive spark-ignition engine fuel (ASTM D4814) and the ASTM standard for denatured fuel ethanol for blending with gasolines (ASTM D4806) are mentioned in EPA regulations and provide guidance on the properties considered to be important in evaluating spark-ignition fuels. The standards, detailed in Section 4.2, specify such factors as vapor pressure, corrosiveness, and permissible levels of impurities, and are used here as a starting point for evaluating the functionality of higher alcohols as fuels in spark-ignition vehicles.

**How will these oxygenates affect the durability of the engine and the emissions control systems?** To answer this question, issues of materials compatibility must be addressed, as must questions regarding the effect of oxygenates on the temperatures and makeup of gases in contact

with a catalytic converter. From a regulatory perspective, the aliphatic alcohols and ethers do not have to demonstrate that they have no effect on emission control system durability as EPA stipulates that they are acceptable at limited concentrations. However, information on their effects on emissions control system durability is limited and it is primarily derived from limited testing on ethanol.

**How will these oxygenates affect emissions?** Currently, light-duty vehicles must meet standards for carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub>), and nonmethane organic gas (NMOG) emissions. In addition to affecting the emissions of these pollutants, a new fuel could cause the emission of different compounds that may have higher or lower toxicities than those from gasoline combustion. To register a new fuel with EPA, a significant body of emission testing data is required.

**Do the storage and transport of the new fuel component represent an environmental hazard if it is spilled or otherwise released to the environment?** This involves questions of human and biological toxicity as well as mobility and biodegradability in the environment.

**Will the new fuel represent a safety hazard in storage, transport, or use?** New fuels must demonstrate compatibility with distribution, storage, handling, and dispensing equipment. Fire safety hazard is also a potential issue. Flammability limits, flash points, and autoignition temperatures are the parameters typically used to determine the level of danger in different situations. Those characteristics are reviewed for these fuels in Section 6.1.

**Can the fuel be transported and stored in the existing gasoline pipelines and storage tanks?** One concern here is the water tolerance of the fuel. The ASTM standard for gasoline (ASTM D4814) provides water tolerance levels that have proven acceptable for other fuel blends. In addition, an Underwriters Laboratories (UL) listing for storage tanks and dispensers, often required for insurance and code compliance purposes, may require that extensive testing be conducted on material compatibility.

While there may be a range of blends that will meet the functional requirements for a spark-ignition fuel, optimizing renewable oxygenate use will depend not only on the properties of the blend, but also on economic and technological aspects related to its production. The production of higher alcohols and other oxygenates is currently an area of intense research and development. This document briefly discusses production processes.

Other important issues such as economics and life-cycle greenhouse gas impacts of renewable oxygenates as a replacement for gasoline must be evaluated as a function of the production method and feedstock and are beyond the scope of this document.

## 2 CHEMICAL STRUCTURE

Alcohols are identified as organic compounds in which a hydroxyl group (-OH) is bound to a hydrocarbon structure. Here we focus on aliphatic alcohols exclusively. The simplest of the alcohols is methanol, which consists of one carbon atom surrounded by three hydrogen atoms and a hydroxyl group (CH<sub>3</sub>OH). Ethanol is the only two-carbon alcohol (C<sub>2</sub>H<sub>5</sub>OH), but as more carbon atoms are added, the hydroxyl group can be attached at various locations in the molecule. Beyond three carbon atoms, the alkyl structure can also vary. The normal (or n-) isomers are also referred to as linear alcohols. Propanol is an alcohol with three carbons and two isomers (Figure 1). Butanol is an alcohol with four carbons and four isomers (Figure 2). Pentanol, which consists of five carbons, has six isomers; however, only n-pentanol and isopentanol (3-methyl-1-butanol) are currently discussed as fuel components (Figure 3).

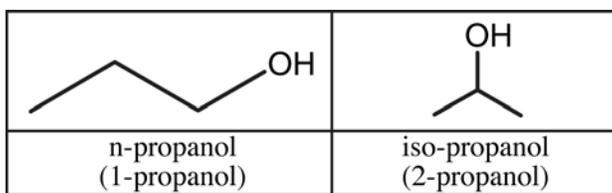


Figure 1. Propanol isomers

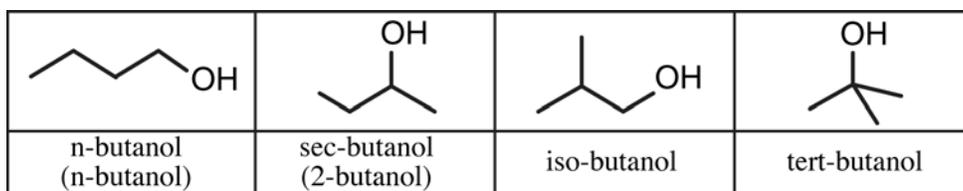


Figure 2. Butanol isomers

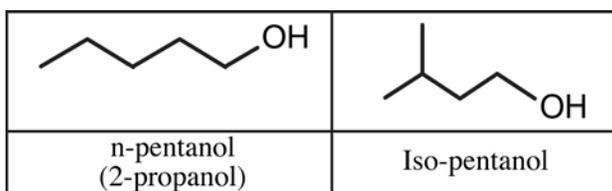


Figure 3. Pentanol isomers

Several other compounds that can be produced from cellulosic biomass and have been proposed as fuels are shown in Figure 4. MTHF is an aliphatic ether consisting of a five-membered ring structure and a methyl group attached on one of the carbons adjacent to the oxygen. DMF has the five-sided ring structure; however, the ring is aromatic, as in a furan molecule. DMF has two methyl groups attached to the ring, one on each carbon adjacent to the oxygen. MF has the same aromatic furan at its core as DMF, but has only one methyl group. GVL is similar to MTHF,

with a double-bonded oxygen bonded to the five-sided ring structure. Levulinic acid (LA) is a keto-acid consisting of five carbons with a ketone group on the fourth carbon, shown here as the ethyl ester, ethyl levulinate. LA can also be converted to pentanoic acid. The final oxygenate considered is the methyl ester of pentanoic acid (PA), MP.

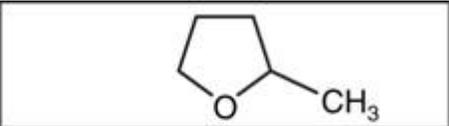
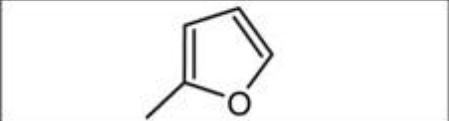
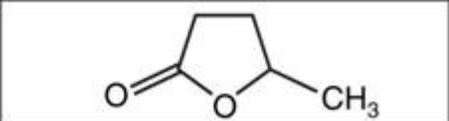
MTHF		EL	
DMF		BL	
MF		MP	
GVL		EP	

Figure 4. Chemical structure of cellulose-derived oxygenates

### 3 PRODUCTION

There are three major pathways for the production of oxygenates from biomass:

- Fermentation of sugar-containing materials by yeast or bacteria
- Gasification of ligno-cellulosic biomass at high temperatures with steam/oxygen to create synthesis gas, followed by catalyzed reaction of the synthesis gas components to mixed alcohols
- Acid hydrolysis (or related approaches) of ligno-cellulosic biomass to produce a range of five-carbon oxygenates, in some cases requiring subsequent reaction with an alcohol such as methanol, ethanol, or butanol.

These processes are in the developmental stage, and many aspects of the process that will impact fuel quality are confidential and may still change. Some important considerations impacting fuel use are:

- What are the co-products and by-products of fermentation or conversion of cellulose to sugars, and will it make sense to include any of these in the fuel or will they all need to be removed? Ethanol will be a co-product of ABE fermentation (so called because it produced acetone, butanol, and ethanol), for example, and might be profitably left in the fuel blending component.
- Particularly for alcohols, what isomers are produced?
- Will there be impurities remaining? Both inorganic and organic impurities can have significant impacts on emissions and other fuel properties.
- How much water will remain in the product stream?

#### 3.1 Alcohols by Fermentation

Fermentation is a process by which microorganisms derive energy from the oxidation of organic compounds. Because the fermentative oxidation process is incomplete, the alcohol products of fermentation retain much of the energy that was in the starting carbohydrate molecules.

Fermentation processes that generate ethanol from carbohydrates, particularly those derived from corn and sugarcane, are well understood and were used industrially to produce 10 billion gallons of ethanol annually in the United States alone in 2009.<sup>1</sup>

Biomass resources in plants and trees are primarily carbohydrates and lignin. Lignin is a complex molecule that is relatively unreactive and difficult to dissolve, so most biomass-to-fuel schemes focus on the carbohydrate portion. Carbohydrates include cellulose and hemicellulose and the simple sugars from which those polymers are built. To date, alcohols have been produced biologically on a commercial scale only from carbohydrate feedstocks.<sup>3</sup>

It is known that propanol can be produced as a by-product of ethanol fermentation<sup>4</sup>; however, evidence of commercial production of propanol from fermentation was not found. The standard procedure for the manufacture of n-propanol and isopropyl alcohol is via petrochemical feedstocks. It is apparent that most of the commercial interest in higher alcohol production via

biological pathways is focused on butanol isomers rather than propanol or any of the longer-chained alcohols.

Biological production of butanol has recently been reviewed by Durre<sup>5</sup> and Arnold.<sup>3</sup> Historically, the primary higher-alcohol compound produced commercially has been n-butanol, but there has also been some work done to produce sec-butanol and isobutanol. During the First World War, industrial quantities of butanol were produced by the ABE fermentation process. Acetone was the intended product, but eventually various industrial uses were developed for the huge quantities of butanol produced. However, in the latter half of the 20<sup>th</sup> century, production of butanol through this process declined and was replaced by petrochemical-based processes.

Recently, the production of butanol from biomass has received new attention, with a focus on developing novel biological pathways and process changes to reduce costs. Although both ethanol and butanol are toxic to the organisms that make them, ethanol can be produced at concentrations that top out between 10% and 18%; butanol fermentation is inhibited at much lower concentrations. Typically, traditional ABE fermentation can produce only 2 wt% butanol.<sup>6</sup> Several companies are working to commercialize improved processes for making butanol, in several cases targeting isobutanol because of its higher octane number.<sup>7,8,9,10,11,12</sup> We are not currently aware of a method for producing tert-butanol from biomass.

### **3.2 Alcohols via Synthesis Gas**

Another approach for the production of alcohols from biomass is via synthesis gas. Synthesis gas is CO and hydrogen (H<sub>2</sub>) that can be generated from biomass or from any carbon-containing material. In addition to biomass, municipal waste and used tires have also been considered as feedstocks. Synthesis gas can also be formed from coal or natural gas. The ability to produce mixed alcohols from synthesis gas has been known for more than a hundred years. Reaction kinetics typically favor methanol at high conversion, and methanol is largest single component of the mixed alcohol product. Operation at lower conversion of up to 30% leads to improved selectivity to C<sub>2</sub> and higher alcohols.<sup>13,14</sup> Current research focuses on improving catalysts and optimizing reactor design to improve selectivity for specific products and increase product yields. The current state of mixed alcohol production from synthesis gas is reviewed in two recent articles and a recent report.<sup>15,16,17</sup>

Numerous companies claim to be developing processes to produce alcohols from synthesis gas.<sup>18,19,20</sup> A detailed process design with an economic evaluation was recently published.<sup>17</sup> Different estimates of the relative concentration of alcohols produced have been made for the different processes (Table 1). EPA's "substantially similar" rule (discussed below) allows only up to 0.3 vol% methanol, or 2.75% methanol if an equal volume of butanol or other higher alcohols is also present, although waivers to the rule allowing up to 5% methanol with 2.5% higher alcohols have been granted.

The expected proportion of higher alcohols (propanol and above) is in the 10%–20% range. The National Renewable Energy Laboratory (NREL) process was developed for the purpose of making ethanol, and its high ethanol percentage can perhaps be explained by the choice of process design, catalyst, and reaction conditions that are intended to produce ethanol. Methanol production is kept low by recycling methanol within the process. The "others" listed in Table 1

are primarily short straight chain alkanes that could be removed in the purification phase of the process,<sup>21</sup> although they might be acceptable in the finished gasoline.

**Table 1. Products from mixed alcohol synthesis via synthesis gas**

	<b>Typical Product</b> <sup>22,23,24</sup>	<b>NREL Model</b> <sup>17</sup>
Methanol	30%–70%	5.01%
Ethanol	35%–45%	70.66%
Propanol	7%–15%	10.07%
Butanol	1%–7%	1.25%
Pentanol+	1.5%–2%	0.17%
Acetates (C <sub>1</sub> and C <sub>2</sub> )	2%–4%	
Others	1%–10%	10.98%
Water <sup>a</sup>	2%	1.86%

<sup>a</sup> Water would likely be limited to 1% in the mixed alcohol/gasoline blendstock.

Propanol and higher alcohols exist in various isomeric forms, and the isomers have different properties. Thus, it is important to know the isomer makeup of the product stream. In many processes, catalyst selection appears to have been made based on selectivity for linear alcohols. However, branched alcohols will exhibit somewhat higher octane numbers and thus might offer some economic advantage.

Any sulfur in the feedstock is reduced in the gasification reactor to hydrogen sulfide (H<sub>2</sub>S) and carbonyl sulfide (COS), which is then further treated to remove elemental sulfur as a waste product. However, molybdenum sulfide-based catalysts require a low concentration of sulfur in the synthesis gas to maintain catalyst activity. Christensen et al. found as much as 340 parts per million (ppm) sulfur in their mixed alcohol product, primarily in the form of thiols.<sup>25</sup> In January 2006, the allowable sulfur content of gasoline in the United States was reduced to an average of no more than 30 ppm. Keeping sulfur content low will be an important issue if the alcohol product is used as a vehicle fuel.

Organic co-products are another issue that may impact the use of synthesis gas products as fuels. Small concentrations of other organic compounds may have significant impacts on the products of combustion and consequent emissions from engines using these mixtures as fuels. While the models suggest a relatively limited range of compounds in the products, experience suggests that the combination of CO and H<sub>2</sub> and high-temperature reaction conditions might lead to a range of organic impurities in low concentrations.

### 3.3 Cellulose Hydrolysis

Ligno-cellulosic biomass consists of cellulose (a polymer of glucose, a six-carbon sugar), hemicellulose (a polymer of both six- and five-carbon sugars), and lignin (a complex biopolymer that is highly aromatic in nature). Figure 5 shows a simplified scheme for reaction of a six-carbon sugar, or hexose, with acid and water (acid hydrolysis) to form hydroxymethyl furfural (HMF). This compound can be converted to DMF by hydrogenation over a copper-ruthenium catalyst.<sup>26</sup> HMF can be converted to LA by further acid treatment to cause hydration and loss of one carbon as formic acid. LA can be converted to esters by reaction with alcohol (esterification). These esters have been proposed as both diesel and gasoline blending components.

LA can be converted to GVL by hydrogenation, and GVL in turn can be converted to MTHF by further hydrogenation. Horvath et al. have proposed the use of GVL as a fuel.<sup>27</sup> Hydrogenation of GVL under different conditions with a different catalyst leads to the production of PA, which can be converted to MP by reaction with alcohols. MTHF and MF can also be produced from the pentoses (five-carbon sugars) in hemicellulose via furfural<sup>28</sup> as shown in Figure 6.

However, the U.S. Department of Justice lists GVL as an addictive drug subject to abuse by ingestion. It is part of a family of drugs, the most well-known of which is  $\gamma$ -hydroxybutyrate (GHB), more commonly known as the “date rape drug.” GVL, GHB, and the other GHB analogs cause relaxation, mild euphoria, and drowsiness; may increase libido, suggestibility, and passivity; and cause amnesia. GVL is physically addictive, causing addicts to experience severe withdrawal symptoms if they miss a dose or attempt to stop using the drug.<sup>29</sup> As with many potentially abusable compounds, GVL has avoided regulation to this point because it is relatively rare. However, should it become widely available, it would likely be regulated very strictly. MP also has drug-related uses, although it is not regulated as such in the United States. It is a mild sedative and used as a fragrance and in cosmetics.

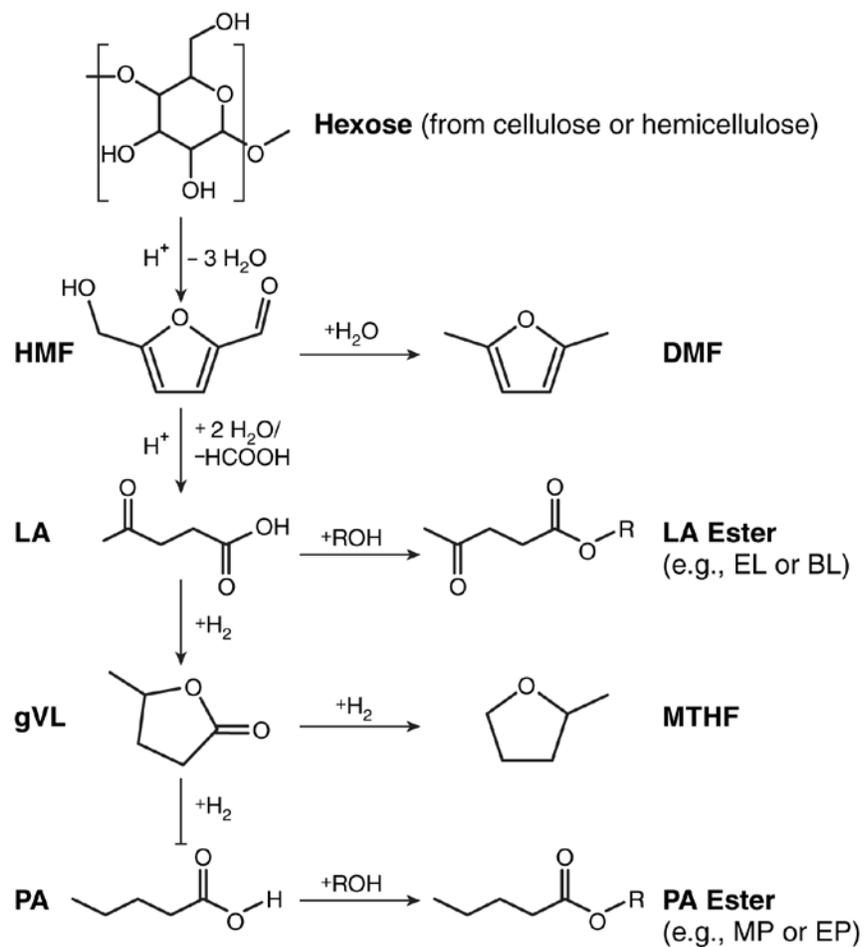
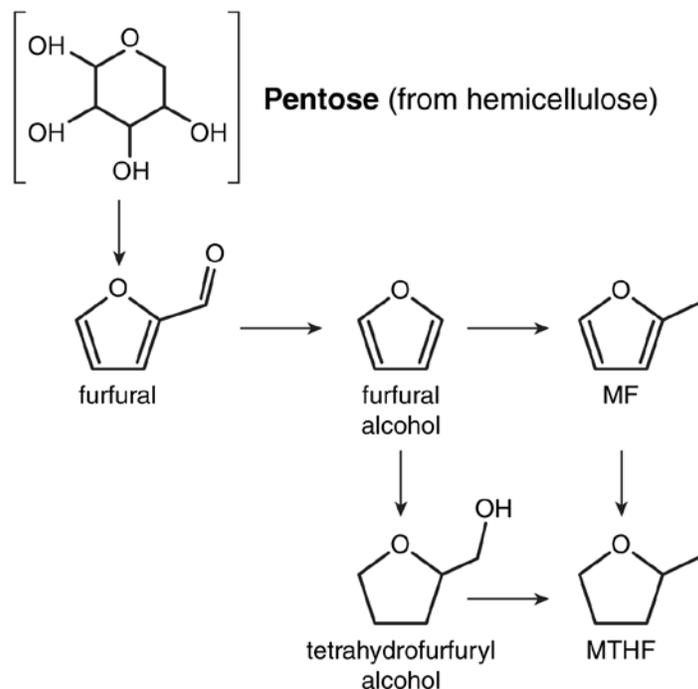


Figure 5. Simplified scheme showing conversion of C<sub>6</sub> sugar (as in cellulose) to cellulose-derived oxygenates (after Palkovits,<sup>30</sup> Lange et al.,<sup>31</sup> and Alonso et al.<sup>32</sup>).



**Figure 6. Simplified scheme showing conversion of C<sub>5</sub> sugar (pentose as in hemicellulose) to cellulose-derived oxygenates**

Two other furanic compounds, ethoxymethyl furfural (EMF) and acetoxymethyl furfural (AMF), have been proposed as a fuel or fuel additive by Avantium in its patent for the synthesis of 5-alkoxymethyl furfural ethers and their use.<sup>33</sup> Avantium proposes manufacturing these compounds via HMF from hexose. There is little information about these compounds other than that provided by Avantium, which estimated that EMF has an energy density very close to that of gasoline, 113,000 Btu/gal for EMF vs. about 110,000 Btu/gal for AMF. Neither compound is listed in the *CRC Handbook of Chemistry and Physics*<sup>34</sup> or Lange's *Handbook of Chemistry*.<sup>35</sup> One source<sup>36</sup> lists AMF's melting point as 53°C–55°C and its flash point as 108°C. Assuming these values are true, it is a solid at room temperature and thus is not appropriate as a gasoline substitute. Because of the lack of publicly available information about these compounds, they are not discussed further.

## 4 REGULATIONS AND STANDARDS

There is a wide range of federal and state regulatory requirements that must be met before widespread introduction of any new spark-ignited engine fuel. These are summarized by Sierra Research in a report for the American Petroleum Institute (API).<sup>37</sup> The following requirements are listed:

- Compliance with Clean Air Act Section 211(f) that fuels be substantially similar to unleaded gasoline;
- Registration of the fuel with EPA;
- Changes to EPA's Reformulated Gasoline (RFG) regulations;
- Changes to EPA's Gasoline Detergent Additive regulations;
- Changes to the Clean Air Act and EPA regulations if the Reid vapor pressure (RVP) allowance granted to E10 is to be provided to other oxygenate blends;
- Changes to federal fuel rating and labeling requirements;
- Changes to ASTM and National Institute of Standards and Technology (NIST) specifications for commercial fuels;
- Changes to a myriad of state fuel requirements, with the number and nature of those changes varying from state to state; and
- Changes in equipment and operating practices in the gasoline transportation and distribution system, including pipelines, storage tanks, and retail dispensing facilities.

However, in support of new biofuels, the Energy Independence and Security Act of 2007 mandated a significant increase in the amount of biofuels in the nation's fuel supply to 36 billion gallons per year by 2022 from only 4.7 billion gallons in 2007. There is a further requirement that a minimum of 21 billion gallons of this requirement be met by advanced biofuels, which are defined as renewable fuels other than corn-based ethanol with lifecycle greenhouse gas emissions that are at least 50 percent less than greenhouse gas emissions produced by gasoline or diesel. The fuels considered here have the potential to be considered advanced biofuels, depending upon the production method used.

### 4.1 Federal Requirements

#### 4.1.1 *Substantially Similar Requirement*

Section 206 of the Clean Air Act of 1977 prohibits the introduction of fuel or fuel additives into commerce for use in light-duty motor vehicles that are not "substantially similar" to unleaded gasoline, as defined for at least one of the volatility classes in ASTM D4814-88. In 1991, the EPA provided an interpretive ruling, which specified that "substantially similar" fuel could include up to 2.7% oxygen by weight, from any combination of aliphatic ethers and/or alcohols, excluding methanol.<sup>38</sup> This was a change from an earlier ruling on "substantially similar" fuels<sup>39</sup> that allowed only up to 2.0% oxygen by weight.

In addition, under Section 211(f)(4) of the Clean Air Act Amendments, the EPA is permitted to grant waivers for additives and fuels that do not meet the definition of "substantially similar" if

the applicant demonstrated that the fuel in question did not “significantly deteriorate or contribute to the deterioration of the performance of any motor vehicle emissions control system.” Several of the waivers granted are applicable to alcohol fuels and are listed in Table 2 with the appropriate Federal Register (FR) reference. These waivers were all granted in the 1980s. Notable are waivers allowing 10 vol% ethanol (nominally 3.5% oxygen) and higher alcohols at up to 3.7% oxygen (the “Octamix waiver”).

Of the non-alcohol compounds included here, only MTHF would be considered substantially similar because it is both an aliphatic compound and an ether. MTHF can legally be added to gasoline at concentrations of up to 2.7 wt% oxygen, (14.5 wt% MTHF) under current regulations. None of the other compounds considered meets the definitions of aliphatic ethers or alcohols. DMF and MF are aromatics, while the other compounds (EL, BL, GVL, and MP) are esters (or keto-esters in the case of the levulinates).

For the compounds that do not meet the definition for “substantially similar,” the most likely path for regulatory acceptance as a gasoline additive would be to request a waiver. However, a waiver for a new fuel will likely require a massive testing program. For example, for ethanol blends of 15% and 20% (E15 and E20), which have higher percentages of ethanol than the “substantially similar” ruling or waivers allow, EPA is requiring extensive, full-useful-life durability testing to demonstrate compatibility with emission control systems as well as a large body of other test data.<sup>40</sup>

#### **4.1.2 Fuel Registration and Health Effects Testing**

Code of Federal Regulations (CFR) Title 40, Part 79, (40 CFR 79) “Registration of Fuels and Fuel Additives” specifies that fuels must be registered with EPA before their introduction into commerce. Fuel manufacturers are required to submit basic data such composition, concentration, total annual production volume, and other information. More importantly, EPA requires that fuels meet Tier 1 and Tier 2 testing requirements. Tier 1 involves a literature search on health and welfare effects as well as performance of emissions tests (both combustion and evaporative, if applicable) with detailed emissions speciation. A Tier 2 test is intended to measure the health effects of inhalation of these emissions and typically involves generation of emissions with an engine or vehicle, exposure of laboratory test animals to these emissions, and assessment of the effects of this exposure. A Tier 2 test is a major undertaking and can take years to complete and potentially cost several million dollars.

None of the long-chain alcohols or other oxygenates described in this report has completed Tier 1 or Tier 2 testing. Gevo is in the first phase of Tier 1 testing for isobutanol, according to its August 2010 filing with the Securities and Exchange Commission.<sup>41</sup> Butamax also claims to be working on health effects testing of isobutanol to meet EPA requirements.<sup>42</sup>

#### **4.1.3 Other Federal Requirements**

Gasoline and diesel fuel ratings and labeling are administered by the Federal Trade Commission under 16 CFR 306 for fuel labeling and potentially also for fuel rating requirements will be necessary for new fuels. Material safety data sheet requirements in 29 CFR 29 1910, Section 1200 may also require modification.

**Table 2. Substantially Similar Fuel Blends and Fuel Blends with Waivers**

<b>Compound</b>	<b>Regulatory Basis</b>	<b>Maximum Oxygen Wt%</b>	<b>Maximum Allowable Vol%</b>
Methanol	“Substantially similar”		0.3
Denatured ethanol	47 FR 14596	3.5	10.0
Propanol and isomers	“Substantially similar”	2.7	9.6
Butanol and isomers	“Substantially similar”	2.7	11.5
Pentanol and isomers	“Substantially similar”	2.7	13.4
Hexanol	“Substantially similar”	2.7	15.6
Methanol and butanol (or other higher molecular weight alcohol) in equal volumes	“Substantially similar”	2.1, if half methanol, half butanol	5.5 total, equal amounts of methanol and higher alcohol
Mixtures of alcohols and ethers, not including methanol	“Substantially similar”	2.7	Varies
ARCO Oxinol™ – combination of methanol and t-butanol and small amounts of butanes, water, and other oxygenated compounds	46 FR 56361	3.5	Up to 4.75% methanol, 4.75% t-butanol in equal amounts
ARCO Arconol™ – combination of t-butanol and small amounts of butanes, acetone, water, peroxide, and other oxygenated compounds	46 FR 56361	3.5	Up to 16% t-butanol
DuPont – methanol and higher alcohols, must include corrosion inhibitor	50 FR 2615, 52 FR 18736	3.7	5% methanol, 2.5% higher alcohols
Texas Methanol Corp. (Octamix waiver) – methanol and higher alcohols, must include corrosion inhibitor	53 FR 3636, 53 FR 17977, 53 FR 43768	3.7	Maximum 5% methanol, minimum 2.5% higher alcohols

EPA also mandates the addition of detergent additives to gasoline to prevent deposit formation in engines and fuel systems. In 40 CFR 80, Subpart F, EPA specifies the procedures and test fuels for detergent certification. The rule requires testing with gasoline containing 10% ethanol and all existing certifications for detergent additives are for fuels containing no more than 10% ethanol. Changes to these regulations are required to specify testing procedures and fuels for other oxygenates, and then these procedures must be used to certify suitable detergents for use in new fuels.

Addition of 10% ethanol to gasoline typically increases the vapor pressure by 1 psi (6.9 kPa). The Clean Air Act provides a 1-psi exemption for non-RFG during the summer. Should any new oxygenate increase gasoline vapor pressure, this 1-psi exemption would not apply unless changes are made to the Clean Air Act to provide such an exemption. EPA requires the use of RFG in many parts of the country that are not in compliance with air quality standards or that are working to maintain compliance. RFG must meet pollutant emissions requirements that are estimated using U.S. Environmental Protection Agency's Complex Model. RFG accounted for roughly 35% of U.S. gasoline sales in 2009.<sup>43</sup> Oxygenates other than ethanol (at up to 10%) are not included in the Complex Model and thus changes to the model and potentially to the RFG regulations would be required to accommodate other oxygenates.

## **4.2 State Requirements**

### **4.2.1 *ASTM and NIST Specifications***

EPA requires that all gasoline and gasoline-oxygenate blends (including alcohols and ethers) sold in the United States meet the requirements of ASTM Standard D4814-88. However, many states have adopted more recent (or the most recent) versions of this specification as part of consumer protection laws or alternatively have adopted model laws and regulations developed by the National Council on Weights and Measures under NIST. The NIST model or uniform regulations are based on D4814 but may provide relief from certain provisions, especially for blending of up to 10% ethanol.

ASTM D4814 was developed to ensure that its requirements are primarily functional specifications, not concentrations or formulations. Thus, D4814 does not specifically exclude any oxygenates as long as gasoline remains the primary component of the fuel and the performance requirements of the specification are met. Table 3 presents properties and limits specified in ASTM D4814. As performance-based specifications, these properties are all applicable to blends of higher alcohols and other oxygenates with gasoline. The reasons for their inclusion in the standard are listed in the third column of Table 3. Very little data exist on how blending higher alcohols or other oxygenates with gasoline or unfinished gasoline (blendstock for oxygenate blending) affects the D4814 properties. Furthermore, the Driveability Index (DI) is not defined for fuels other than hydrocarbons or hydrocarbon-ethanol blends up to 10%. The impact of higher alcohols and cellulose derived oxygenates on driveability should be assessed.

Although material compatibility is also anticipated to be less of an issue for higher alcohols than it is for ethanol, materials compatibility testing for the other oxygenates will likely be required before widespread use.

**Table 3. ASTM 4814-10b, Chemical and Physical Properties of Spark-Ignition Fuels**

Property	Limit	Rationale
Maximum vapor pressure at 37.8°C (100°F).	Wide range of requirements depending on the location and time of year, 54 kPa (7.8 psi) to 103 kPa (15.0 psi) maximum	Minimize volatile organic compound losses to atmosphere and ensure acceptable driveability
Distillation temperatures for T <sub>10</sub> , T <sub>50</sub> , T <sub>90</sub> , T <sub>100</sub> °C (°F)	Varies depending upon location and time of year T <sub>10</sub> max: 50°C – 70°C (122°F – 158°F) T <sub>50</sub> min: 66°C – 77°C (150°F – 170°F) T <sub>50</sub> max: 110°C – 121°C (230°F – 250°F) T <sub>90</sub> max: 185°C – 190°C (365°F – 374°F) T <sub>100</sub> max: 225°C (437°F)	Ensure reliable startup and driveability and prevent blending of heavy components that could lead to engine deposits
Distillation residue	2 vol% maximum	Prevent blending of heavy components that could lead to engine deposits
Maximum Driveability Index: DI = 1.5 T <sub>10</sub> + 3.0 T <sub>50</sub> + 1.0 T <sub>90</sub> + 1.33* ethanol volume%	From 569 to 597 maximum (unitless), depending on location and time of year	Reliable cold-start and driveability in cold temperatures immediately after startup
Minimum temperature at which the vapor-liquid ratio is 20	Range of requirements depending on the location and time of year, from 35°C (95°F) to 60°C (140°F)	Prevent vapor lock and carburetor icing
Copper Strip Corrosion Test, 3 hours at 50°C (122°F), maximum	No. 1	Minimize corrosion of copper and other metal-containing engine parts
Silver Strip Corrosion Test, 3 hours at 50°C (122°F), maximum	1	Minimize corrosion of silver and other metal-containing engine parts
Oxidation stability, minimum	240 minutes	Minimize deposits
Lead content, maximum	(For unleaded fuel) 0.013 g/L (0.05 g/gal)	Lead is a highly toxic air pollutant and catalyst poison
Sulfur content, maximum	(For unleaded fuel) 0.0080 mass%	Inhibits activity of the 3-way catalyst and leads to formation of particulate matter
Solvent-washed gum content, maximum	5 mg/100 mL	To avoid deposits on carburetor, fuel injectors and intake valves
Water tolerance of alcohol blends – maximum temperature at which phase separation occurs	No specification but suitable for location and time of year	Ensure that the fuel does not separate into aqueous and gasoline phases
Anti-Knock Index: AKI = (RON+MON)/2	Recommended 87 to 91, depending upon vehicle, with waiver of up to 5.5 AKI units depending on altitude and local climate	Prevent knocking

Note: MON = motor octane number; RON = research octane number.

Any new oxygenate commonly used for blending with gasoline would likely be required to have a blendstock specification to ensure consistent quality in the marketplace. ASTM Standard D4806 covers fuel ethanol that is intended for use as a blend with gasoline at concentrations of between 1% and 10%. Although the standard is not applicable to higher alcohols or other oxygenates used as gasoline blend components, it is considered here as guidance on properties that may be important. Fuel ethanol is denatured, usually with gasoline or natural gasoline, to make it unfit for human consumption. Other oxygenates that have the potential for human ingestion as drugs (GVL and MP) may also eventually require denaturing if produced in large quantities. Denaturing is not necessary for other oxygenates; therefore, a number of properties associated with the denaturant would not be applicable. The properties specified in D4806 and the reason for each are listed in Table 4.

#### **4.2.2 Other State Requirements**

A wide range of fuel requirements exists in various state laws and may need to be updated or changed to accommodate higher alcohols or cellulose-derived oxygenates. These include:

- Ethanol blending mandates. It may not be possible to blend an EPA-compliant fuel using other oxygenates in states that have ethanol blending mandates because the total oxygenate content would be above the level allowed by the “substantially similar” rule.
- Offsets to T<sub>50</sub> and vapor lock protection requirements. Many states have adopted allowances to encourage ethanol blending. It is not clear how these will impact other oxygenates.
- California fuel requirements. California has a long list of unique fuel requirements that may or may not be met by other oxygenates.
- Compliance with State Implementation Plans. To come into compliance with air quality standards, many states have adopted fuel vapor pressure requirements more restrictive than required by EPA or ASTM Standard D4814. In addition, new oxygenates may impact pollutant emissions in ways that require states to modify their state implementation plans.

#### **4.3 Transportation and Distribution System Requirements**

The introduction of a new fuel oxygenate will bring up practical issues such as how to move the fuel or fuel blends to market and how to handle them at truck terminals. Pipeline transport of a new gasoline/oxygenate blend is theoretically possible for oxygenates that will not phase separate in the presence of water. However, there appears to be no established procedures for demonstrating water tolerance or compatibility with pipeline infrastructure. Significant large-scale testing is likely required to prove that a new fuel can be transported. A second issue is the availability of storage tanks. If a terminal is handling ethanol, there may not be additional storage tanks available for a new oxygenate.

**Table 4. ASTM D4806-11, Chemical and Physical Properties for Denatured Fuel Ethanol for Blending with Gasoline**

<b>Property</b>	<b>Limit</b>	<b>Rationale</b>	<b>Applicable to Other Oxygenates?</b>
Ethanol, volume %, min <sup>a</sup>	92.1	Ensure that fuel additive is primarily ethanol.	It is likely a higher min volume % would be required because no denaturant is needed.
Methanol, volume %, max	0.5	Lowers water tolerance of the fuel and increases the vapor pressure.	May apply, although value may be different because higher alcohols improve water tolerance of methanol/gasoline blends.
Solvent-washed gum, mg/100 mL, max	5.0	Insoluble gums can clog filters and deposit inside the fuel system.	Yes.
Water content, volume %, max	1.0	Ensure water tolerance.	Yes, if water is soluble at levels above 1 volume percent.
Denaturant content, volume %, min <sup>a</sup>	1.96	Denaturant is required to prevent human consumption of ethanol.	No, other oxygenates do not require denaturants.
Denaturant content, volume %, max	2.5 <sup>a</sup> or 5.0	Too much denaturant dilutes the ethanol content.	No, other oxygenates do not require denaturants.
Inorganic chloride content, mass ppm (mg/L), max	10 (8)	Chloride is corrosive to many metals.	Yes.
Copper content, mg/kg, max	0.1	Catalyst for oxidation of hydrocarbons and can increase gum formation.	Yes.
Acidity (as acetic acid) mass % (mg/L), max	0.007 (56)	Low-molecular-weight organic acids in aqueous solution are highly corrosive to many metals.	Yes.
pHe	6.5–9.0	pHe above and below these values can cause problems with material compatibility in engines.	pHe is a measurement specific to ethanol; however, a similar measure of acid strength may be required for other oxygenates.
Sulfur, mass ppm, max	30	Can increase tailpipe emissions of particles, inhibits 3-way catalyst.	Yes, D4814 currently limits gasoline to 80 ppm sulfur.
Sulfate, mass ppm, max	4	Can cause deposits and filter plugging as well as fuel injector sticking.	Yes.
Appearance	Visibly free of suspended or precipitated contaminants (clear and bright)	To avoid deposits that can plug filters and clog fuel injectors.	Yes.

<sup>a</sup>The maximum amount of denaturant the IRS considers part of the denatured fuel ethanol for full ethanol blender's tax credit.

The main concerns, however, are related to retail outlets. These are regulated by multiple agencies (Occupational Safety and Health Administration, National Fire Protection Association, and others) whose primary requirements are that the equipment be compatible with the product being stored and dispensed and that the equipment be listed by independent organizations such as UL. UL provides a listing of products that it has tested as being safe for use in specific applications. Local authorities frequently require a UL listing to demonstrate compliance with fire safety codes and environmental protection regulations. UL lists these products for use with specific fluids, for example, current dispensers are listed for use with gasoline-ethanol blends containing up to 10% ethanol. Typically manufacturers submit their equipment to UL for testing using a test protocol that is defined and published by UL and includes specific test fluids that are intended to simulate worst case use scenarios. It is likely that retail sale of any of the oxygenates discussed in this report would require testing to determine compatibility with a range of equipment, including:

- Hanging hardware (nozzles, hoses, breakaways, and swivels)
- Dispensers
- Product pumps
- Underground storage tanks
- Leak detection systems
- Vapor recovery systems
- All associated piping.

## **5 CHEMICAL PROPERTIES**

### **5.1 Alcohols**

Various properties of alcohols and gasoline are compared in Table 5. While gasoline and diesel are mixtures of a variety of compounds and thus can exhibit a range of properties, many of those properties are limited by federal regulation and ASTM specifications. In contrast, alcohols are singular compounds with specific chemical properties. Note that the properties of various isomers with the same chemical formula may differ significantly.

### **5.2 Cellulose-Derived Oxygenates**

The properties of the oxygenates are listed in Table 6. These data were compiled from a wide range of reference sources. The source of each value is listed below the table and should be considered prior to applying these values.

**Table 5. Chemical and Physical Properties of Gasoline and Alcohols**

Compound	Gasoline	Ethanol	n-Propanol	i-Propanol	n-Butanol	i-Butanol	s-Butanol	t-Butanol	n-Pentanol	i-Pentanol
CAS Number		64-17-5	71-23-8	67-63-0	71-36-3	78-83-1	78-92-2	75-65-0	71-41-0	125-51-3
Formula		C <sub>2</sub> H <sub>6</sub> O	C <sub>3</sub> H <sub>8</sub> O	C <sub>3</sub> H <sub>8</sub> O	C <sub>4</sub> H <sub>10</sub> O	C <sub>5</sub> H <sub>12</sub> O	C <sub>5</sub> H <sub>12</sub> O			
Lower heating value (MJ/kg)	41–44	26.8	30.7	30.4	33.2	33.1	32.9	32.7	34.8	35.4
Lower heating value (MJ/L)	30-33	21.4	24.7	24.1	26.9	26.6	26.7	25.9	28.5	28.3
Latent heat of vaporization (kJ/kg)	352	919.6	792.1	756.6	707.9	686.4	671.1	527.2	647.1	617.1
Lower flammability limit (%)	1.4	3.28	2.13	2.02	1.45	1.68	1.7	2.4	1.2	1.2
Upper Flammability limit (%)	7.6	18.95	13.50	11.80	11.25	10.9	9.0	8.0	10.5	9
Vapor pressure at 20°C (kPa)	50–100	5.8	2	4.4	0.58	1.2	1.7	4	0.6	0.4
Reid Vapor Pressure, (kPa)	54–103	16.0	6.2	12.4	2.2	3.3	5.3	12.2	0.83	1.0
Autoignition temp (°C)	257	363	371	456	343	415	405	478	320	350
Flash point closed cup (°C)	-43	13	15	12	29	28	24	11	43	45
Boiling point (°C)	27–225	78	97.2	82.3	117.7	107.9	99.6	82.4	137.8	132
Melting point (°C)	-40	-114	-126.2	-88.5	-89.3	-108	-114.7	26	-78.2	-117
RON	88-98	109	104*	106	98*	105*	105*	105	(78)	(94)
MON	80-88	90	89*	99	85*	90*	93*	89	(74)	(84)
Viscosity 20°C (cSt)	0.37–0.44	1.5	2.7	3.1	3.6	8.3	4.7	4.2	5	5
Specific gravity, 20°C	0.69–0.79	0.794	0.804	0.789	0.810	0.802	0.808	0.791	0.816	0.8
Solubility of water in compound at 20°C (wt%)	negligible	miscible	miscible	miscible	20.1	20.0	60	miscible	10.6	9.8
Solubility of compound in water at 20°C (wt%)	negligible	miscible	miscible	miscible	7.7	8.7	12.5	miscible	2.2	2.5

Notes on sources for Table 5:

1. Properties for gasoline are from API.<sup>44</sup> Specific gravity of gasoline at 15°C.
2. Lower heating values calculated from information in Willhoit and Zwolinski.<sup>45</sup>
3. All safety data (flammability limits, autoignition temperatures, flash points) for alcohols are from Perry's *Standard Tables and Formulas for Chemical Engineers*.<sup>46</sup> Different values for some of these parameters were found in the *Industrial Solvents Handbook*.<sup>47</sup>
4. All boiling points, melting points, and heats of vaporization are from Willhoit and Zwolinski.<sup>45</sup>
5. Octane numbers for ethanol and tert-butanol are from Hunwartz.<sup>48</sup> Slightly different values are referenced in Popuri and Bata.<sup>49</sup> Octane numbers for isopropanol are from Unzelman et al.<sup>50</sup> Values with \* were measured by NREL using ASTM D2699 and ASTM D2700. Values in parentheses are blending octane numbers measured by NREL using ASTM D2699 and ASTM D2700.
6. Viscosity values for alcohols are from the *Industrial Solvents Handbook*,<sup>47</sup> note that values for t-butanol and i-pentanol are at 25°C.
7. Specific gravity values for alcohols are from the *CRC Handbook of Chemistry and Physics*.<sup>34</sup>
8. Solubility of water in alcohol values are from the *Industrial Solvents Handbook*,<sup>47</sup> except values for pentanol isomers, which were measured by NREL using Karl Fischer titration after saturation with water at 20°C. Solubility of alcohol in water values are from the International Program on Chemical Safety.<sup>51</sup>
9. Reid vapor pressure (RVP, vapor pressure measured at 100°F [37.8°C] measured in a vessel with a vapor/ liquid volume ratio of 4:1 using a specific procedure) measured using ASTM D6378 by Andersen et al.,<sup>52</sup> with the exception of i-pentanol, which was measured by NREL using ASTM D5191, and n-pentanol where RVP was calculated from compound-specific coefficients for the Antoine equation given in Lange's *Handbook of Chemistry*.<sup>35</sup>

**Table 6. Chemical and Physical Properties of Biofuels Compared to Gasoline**

Compound	Gasoline	MTHF	DMF	MF	EL	BL	MP	GVL
		2-Methyl-tetra-hydrofuran	Dimethyl-furan	2-Methyl-furan	Ethyl Levulinate	Butyl Levulinate	Methyl Pentanoate	$\gamma$ -Valero-lactone
CAS Number		96-47-9	625-86-5	534-22-5	539-88-8	2052-15-5	624-24-8	108-29-2
Formula		C <sub>5</sub> H <sub>10</sub> O	C <sub>6</sub> H <sub>8</sub> O	C <sub>5</sub> H <sub>6</sub> O	C <sub>7</sub> H <sub>12</sub> O <sub>3</sub>	C <sub>9</sub> H <sub>16</sub> O <sub>3</sub>	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>
Lower heating value (MJ/kg)	41–44	32.8	33.8	31.2	24.3	27.4	28.6	24.2
Lower heating value (MJ/L)	30-33	28.2	30.1	27.6	24.8	27.1	25.9	26.2
Latent heat of vaporization (kJ/kg)	352	375.3	330.5	358.4	306.7	277.5	371.5	543.9
Lower flammability limit	1.4%	1.5%	--	1.9%	--	--	--	--
Upper flammability limit	7.6%	8.9%	--	14%	--	--	--	--
Vapor pressure at 20 °C (kPa)	50–100	13.6	--	18.5	0.01 @ 17°C	--	1 @ 19°C	--
Reid Vapor Pressure, (kPa)	54–103	--	13.4	18.5	2.1	--	4.0	--
Autoignition temp (°C)	257	270	286	450	425	--	--	--
Flash point closed cup (°C)	-43	-11	16	-22	90	79	22	96
Boiling point (°C)	27–225	78	94	64.7	206	237.5	126	218–220
Melting point (°C)	-40	-136	-63	-91	<-82	-22.6	-91	-12.5
RON	88–98	86	119	103	110	(98)	(105)	100
MON	80-88	73	--	86	102	(96)	(105)	100
Viscosity 20°C (cSt)	0.37–0.44	1.52	--					
Specific gravity (20°C)	0.69–0.79	0.855	0.8883	0.9132	1.0111	0.9735	0.8947	1.0794
Solubility of water in compound, % v/v at 20°C	negligible	5.1%	--	--	8.5 wt%	2.6 wt%	--	miscible
Solubility of compound in water, (%v/v)	negligible	12.1%	0.26%	0.3%	15.2 wt%	1.3 wt%	0.1%	miscible

Notes on sources for Table 6:

1. Properties for gasoline are from API.<sup>44</sup> Specific gravity of gasoline at 15°C.
2. Lower heating values in italics estimated using Dulong formula: gross heating value (kJ/kg) = 337 C + 1442 (H - O/8) + 93 S where C is the mass fraction of carbon, H is the mass fraction of hydrogen, etc. Corrected to net heating value by subtracting the latent heat of vaporization of water at 20°C.
3. Blending RON or MON in parentheses.
4. MTHF – heating value (ASTM D240), RON and MON (ASTM D2699 and ASTM D2700) measured by NREL; boiling point, specific gravity from CRC *Handbook of Chemistry and Physics*<sup>34</sup>; flash point from Lewis<sup>53</sup>; all other properties from Penn Specialty Chemicals, Inc.<sup>54</sup>
5. DMF – heating value, solubility in water, RON from Roman-Leshkov et al.<sup>26</sup>; flash point, boiling point, melting point from Lewis<sup>53</sup>; specific gravity from CRC *Handbook of Chemistry and Physics*<sup>34</sup>; latent heat of vaporization and auto-ignition temperature from uncited data in Zhong.<sup>55</sup>
6. MF – specific gravity, boiling point, melting point from CRC *Handbook of Chemistry and Physics*<sup>34</sup>; flash point and vapor pressure from Lewis<sup>53</sup>; RON and MON from Unzelman et al.<sup>50</sup>; heat of vaporization from Ribeiro da Silva<sup>56</sup>; other properties from Penn Specialty Chemicals.<sup>57</sup>
7. EL – boiling point, specific gravity and solubility from Cox and Dodds<sup>58</sup>; melting point (ASTM D5972), flash point (ASTM D93), lower heating value (ASTM D240), solubilities measured by NREL; heat of vaporization from ChemSpider<sup>59</sup>; autoignition temperature from ChemCAS<sup>60</sup>; RON from Huber et al.<sup>28</sup>; MON from Fitzpatrick<sup>61</sup>; vapor pressure from Merck.<sup>62</sup>
8. BL – boiling point and specific gravity from CRC *Handbook of Chemistry and Physics*<sup>34</sup>; melting point (ASTM D5972), flash point (ASTM D93); lower heating value (ASTM D240), solubilities measured by NREL; heat of vaporization from ChemSpider<sup>63</sup>; blending RON and MON measured at NREL (ASTM D2699 and ASTM D2700); vapor pressure from Merck.<sup>64</sup>
9. MP – latent heat of vaporization from NIST Chemistry Webbook<sup>65</sup>; vapor pressure, boiling point, melting point, specific gravity from CRC *Handbook of Chemistry and Physics*<sup>34</sup>; flash point from Sigma-Aldrich<sup>66</sup>; solubility from NOAA<sup>67</sup>; vapor pressure from Merck<sup>64</sup>; blending RON and MON measured at NREL (ASTM D2699 and ASTM D2700).
10. GVL – boiling point, melting point, specific gravity from CRC *Handbook of Chemistry and Physics*<sup>34</sup> (slightly different values included in Horvath et al.<sup>27</sup> although original source not referenced – boiling point 207°C –208°C, melting point -31°C, specific gravity 1.05), all other values from Horvath et al.

## 6 SAFETY AND ENVIRONMENTAL HAZARDS

Safety and environmental considerations are important in the selection of gasoline additives. For example, methyl tert-butyl ether, in common use as an oxygenate additive to gasoline, has recently been phased out because of concerns regarding its widespread occurrence as a groundwater pollutant.<sup>68</sup>

### 6.1 Safety

The danger of fire and explosion from both gasoline and oxygenates in storage will depend on the temperature and the properties of the specific fuel. All of these compounds present serious fire hazards, but because of their chemical dissimilarity, the risks at specific temperatures differ. Tables 5 and 6 above detail temperature-related parameters that determine flammability.

Flammability limits are the range of vapor pressures, typically expressed as a percent of one atmosphere, between which the vapors can burn. Vapors richer (higher in concentration) than the flammability limits do not have a high enough proportion of oxygen to burn, and vapors with concentrations below the flammability limits do not have enough fuel to burn. The flammability limits should be compared with the vapor pressure to determine the likelihood that vapor concentrations will fall within the flammability limits at a given temperature.

Gasoline, MTHF, and MF are volatile (gasoline is much more volatile than the two oxygenates). Fully saturated gasoline and MTHF vapors at 20°C are too rich to burn (see Table 6). At common ambient temperatures, all three are ignitable. In contrast, methanol, ethanol, propanol, and tert-butanol have lower vapor pressures at 20°C, which fall between their upper and lower flammability limits, within the flammable range. Consequently, while the vapor in closed containers of gasoline or MTHF is not flammable, these alcohols would be expected to generate dangerous concentrations of vapors in storage tanks. Conversely, in open containers, where vapor concentrations are generally diluted to well below saturation concentrations, gasoline and MTHF vapors may be present at concentrations within the flammability limits. Some higher alcohols have vapor pressures (at 20°C) that are below their flammability limits and thus cannot reach dangerous concentrations unless temperatures are elevated.

Flammability limits are not known for a number of the other oxygenates; however, their flash points (the temperature at which the saturated vapor pressure equals the lower flammability limit) are known. Below the flash point it is not possible to ignite the vapors. With flash points of over 90°C, the levulinates are not likely to be a significant fire danger; however, DMF (flash point 16°C), MP (flash point 22°C), and MF (flash point -22°C) may produce flammable vapors in typical storage conditions.

Like the flash point, the autoignition temperature assumes fully saturated vapors. The difference is that the flash point is the lowest temperature at which self-sustaining combustion can occur, while the autoignition temperature is the temperature at which combustion will occur, i.e., the temperature at which saturated vapors will spontaneously combust. For all these fuels, the autoignition temperature is well above any normal ambient conditions and unlikely to occur except in a fire or if a container is placed near a heat source. For this reason, these fuels should be handled with extreme care to avoid contact with sparks or other heat sources.

Another safety issue is flame luminosity. Pure methanol and ethanol flames contain very little soot and so are not luminous, which creates a hazard as workers or fuel users may be burned because they cannot see the flame. Adding gasoline to these alcohols imparts luminosity. Higher alcohols may have adequately luminous flames because of their greater carbon content; however, we were not able to identify studies or data sources on this property.

Fuel storage safety issues for low-concentration blends will be similar to those for straight gasoline. While blending of alcohol may increase or decrease vapor pressure slightly depending on the blend level, gasoline blends will still require careful handling as Class I flammable materials.

MTHF is typically supplied with an inhibitor to prevent the formation of thermally explosive peroxides on exposure to air. Stored MTHF and furans must always be tested for peroxide formation prior to heating. Many laboratories dispose of MTHF and furans that have been open for more than 6 months to eliminate the potential for the formation of dangerous levels of peroxides. It is not clear how the safety issues associated with peroxide formation would be addressed if large amounts of MTHF were in widespread use.

## **6.2 Toxicity**

Whether ingested or inhaled, gasoline is toxic and listed as a possible carcinogen. All of the alcohols are somewhat more toxic, and ethanol ingested in liquid form is considered to be carcinogenic according to the International Agency for Research on Cancer (IARC). Recent studies have shown that regular long-term ingestion of liquid ethanol alcohol may cause cancer,<sup>69</sup> but at exposures far above those that would typically be expected for fuel usage. DMF and MF are also potentially quite toxic. Little is known about MTHF; the levulinates and pentanoates are expected to be less of a concern because they are in use as flavorings and scents. Table 7 presents a quantitative comparison of oral toxicity. Ethanol intended for fuel use is made toxic with the addition of a denaturant (usually gasoline) to discourage human consumption.

**Table 7. Oral Toxicity of Gasoline and Various Oxygenates**

Fuel	Oral LD50 <sup>a</sup> (rat or mouse) <sup>53</sup>	Carcinogenic? <sup>70</sup>
Gasoline	18.75 mL/kg or about 14,000 mg/kg <sup>71</sup>	Gasoline is classed as a possible carcinogen and contains benzene, a known carcinogen
Methanol	5,628 mg/kg	Not classified by IARC
Ethanol	7,060 mg/kg	Ethanol “in alcoholic beverages” classed as known carcinogen; however, this presumes high ingestion levels
Isopropanol	5,045 mg/kg	Not classified by IARC
n-Propanol	1,870 mg/kg	Not classified by IARC
n-Butanol	790 mg/kg	Not classified by IARC
sec-Butanol	6,480 mg/kg	Not classified by IARC
Isobutanol	2,460 mg/kg	Not classified by IARC
tert-Butanol	3,500 mg/kg	Not classified by IARC
MTHF	Unknown; Inhalation rat LD50: 6,000 ppm; skin rabbit LD50 4,500 mg/kg	Not classified by IARC
DMF	300 mg/kg	Not classified by IARC
GVL	8,800 mg/kg	Not classified by IARC
EL	Used as food additive	Not classified by IARC
BL	Used as a food additive, >5,000 mg/kg	Not classified by IARC
MP	2,050 mg/kg <sup>b</sup>	Not classified by IARC
MF	167 mg/kg	Not classified by IARC

- a. The amount of compound per kg of animal that, if ingested, will kill 50% of the tested population. Thus, a smaller value implies greater toxicity.
- b. Used in fragrances, soaps, and cosmetics.

### 6.3 Environmental Considerations

Since most of the oxygenates listed in Table 7 are relatively nontoxic and the alcohols are biodegradable,<sup>72</sup> their effect on the environment in the case of spills is expected to be relatively small. Longer chain and more highly branched alcohols are not as readily biodegraded.<sup>73</sup> Butamax, LLC plans to study the fate and transport of isobutanol in the environment as part of its efforts to get isobutanol certified as a fuel additive in California.<sup>42</sup> The other compounds are not well studied. DMF and MF, with their higher toxicities, may present the greatest concern, while the levulinates and pentanoates, commonly used as food additives, flavors or, in the case of methyl pentanoate, as a mild sedative, would be expected to readily biodegrade and have a lesser impact on the environment. The downside of readily biodegradable compounds may be that they may also be relatively unstable in storage prior to use. Note that the high solubility of some

alcohols can lead to greater mobility and potentially more toxic levels in groundwater in comparison to gasoline and the other potential oxygenated additives.

The presence of ethanol in groundwater is known to increase the solubility of other organics. A similar effect would be expected with higher alcohols. This was supported by a study in which the effects of ethanol, isopropanol, and tert-butanol were compared on the solubility of tetrachloroethylene in aqueous solutions. All three alcohols in solution tested at concentrations of about 20% and above acted as cosolvents, increasing the aqueous solubility of tetrachloroethylene. Tert-butanol exhibited the strongest cosolvent effects.<sup>74</sup>

## 7 USE IN SPARK-IGNITION ENGINES

In the near future, the most likely new use of oxygenates will be higher alcohols in low-concentration blends with gasoline, both because they present the lowest legal hurdles and they are believed, for the most part, to be usable in existing cars without affecting the driver's experience. The four most significant areas in which oxygenate/gasoline blends differ from gasoline are as follows:

- Oxygenates have a lower energy density than gasoline, and when blended with gasoline, oxygenates reduce the energy density of the blend approximately in proportion to the amount of oxygen in the compound.
- Because a solution of nonpolar gasoline and relatively more polar oxygenates is non-ideal, even low concentrations of oxygenates in gasoline can change the volatility of the blend in ways that cannot be predicted from the vapor pressure of the components. On the one hand, if the vapor pressure is higher than that of gasoline, the blend can cause increased evaporative emissions and vapor lock on warm days. On the other hand, the use of lower vapor pressure fuels could cause problems starting vehicles on cold days.
- Oxygenate blends may differ in material compatibility with thermosets, thermoplastics, and elastomers and in potential corrosion of various metals used in engines and gasoline storage and handling systems. In addition, if interchanged with petroleum fuels, the oxygenate blends may act as a solvent and dissolve deposits that are otherwise insoluble in the presence of gasoline. The loosened deposits can affect combustion and clog filters.
- The water tolerance of the oxygenates, especially of the shorter chained and more polar alcohols, is quite different from that of gasoline. This can increase the amount of water taken up into the gasoline, and if enough water is present, a second phase will form and oxygenates may preferentially partition into the aqueous phase.

While these four issues apply to all of the oxygenates considered, they apply to a different extent for each compound. Generally, as the proportion of oxygen in the molecule becomes less, it begins to act more like the hydrocarbons in gasoline. For alcohols, the effect of the lone hydroxyl group diminishes as the molecule grows larger and they are more energy dense, less likely to absorb water, are less corrosive, and have less potential to increase vapor pressure. Other potential differences between gasoline and gasoline-alcohol blends include octane, emissions effects, driveability, and viscosity. In low-concentration alcohol/gasoline blends, toxicity, fuel storage safety, and issues related to environmental spills are determined primarily by the predominant gasoline properties.

### 7.1 Energy Density

By definition, oxygenates include oxygen in addition to carbon and hydrogen. Because the carbon-oxygen and hydrogen-oxygen bonds release no energy when the molecule is combusted, on a weight basis oxygenates have a lower energy density than that of the corresponding hydrocarbon. Ethanol's energy density is less than 70% that of gasoline's. However, the longer the alcohol chain, the less the impact of the lone oxygen atom. Thus, butanol, pentanol, and

higher alcohols have specific energies that are much closer to that of gasoline than ethanol. The volumetric energy density of the compounds considered in this document range from 80% to 95% of the energy density of gasoline. DMF is the closest to gasoline (95% of the volumetric energy density). The energy density of any of the butanols is almost 80% of that of gasoline. In practice, this means that vehicles using oxygenate blends in gasoline will require larger fuel tanks or will travel shorter distances between refueling events. It also means that fuel injection equipment may need to be modified to ensure that the proper amount of fuel is metered into the combustion zone.

Cars built since the late 1980s (virtually all the cars on the road today) operate in “closed-loop” mode most of the time. “Closed loop” means that the exhaust oxygen sensor signal is being used to control the amount of fuel the injectors are adding to the intake. If the oxygen sensor output determines that the combustion mixture is getting fuel-rich, it cuts back on the fueling rate. If the mixture is getting lean, it increases the fuel/air ratio. However, some cars start in open-loop mode until the engine warms up, and then switch to closed-loop operation. Others switch into open-loop operation in order to get more power during accelerations. Thus, in addition to not being covered under EPA’s “substantially similar” rule, there are two potential issues regarding the use of oxygenate blends that have oxygen contents above that of E10. First, the range of the closed-loop system might not allow full compensation for high-oxygen-content fuels. The other issue occurs when the car is operating in open-loop mode. In this case, it expects a certain energy content in the fuel, and the addition of large amounts of oxygen-containing fuels can deceive the system.

The energy density of a blend can be calculated as the energy density of the constituents times the proportion in the blend. For example, using low concentrations of n-butanol (equivalent to 2.7% oxygen) in gasoline yields a fuel that has about 97% of the energy density of gasoline alone. For comparison, all modern cars are designed to operate on concentrations of up to 10% denatured ethanol gasoline (3.5% oxygen), which has about 96% of the energy of gasoline alone. Because the energy density can roughly be estimated based on the oxygen concentration, any blend with an oxygen content less than or equal to that of E10 will have an energy density within the range for which modern vehicles have been designed.

## **7.2 Volatility**

As discussed in Section 4.2, ASTM volatility requirements are specified in several ways: as a vapor pressure measured using specific EPA-approved methodology, but essentially the vapor pressure at 37.8°C (100°F); by looking at various points on the distillation curve; by calculating a DI from several points on the distillation curve; and as a function of the point where the vapor-liquid ratio is 20. Varying the vapor pressure affects operability in several important ways, and it also impacts evaporative and permeation emissions not just from the vehicle but in transport, storage, and fueling. Acceptable values for these vapor pressure-dependent properties vary depending on the region of the country and the time of year.

The vapor pressures of pure alcohols, or any of the other oxygenate compounds described here, are too low to easily start cars at moderate to low temperatures. This can be shown by the inability of alcohols to meet the DI in requirement in ASTM D4814. Cars designed to operate on pure ethanol (E100) (actually containing about 7% water) without gasoline are used in warmer

climates<sup>75</sup> where the low vapor pressures will be less problematic for cold starts (although many so-called E100 vehicles have a separate small tank of gasoline for cold starting). New E100 cars have been proposed by Saab<sup>76</sup> and Suzuki<sup>77</sup> for more general use. Saab states that the company will use a small preheater to warm the fuel when starting a cold car. However, with the existing fleet, the low vapor pressure of ethanol and other oxygenates is a significant barrier to widespread use of these fuels in neat form in the short term. With boiling points of about 200°C, close to that of the heaviest components of gasoline (and far higher than ethanol), and flash points of 72°C and 96°C,<sup>78</sup> the levulinates will be difficult to ignite and can only be used in low concentration blends with lighter fuels in spark-ignition engines.

The impact of oxygenates on the vapor pressure of gasoline blends cannot be estimated assuming ideal solution behavior. Andersen and coworkers<sup>52</sup> have reported the vapor pressures of a range of alcohol/gasoline blends, including some dual alcohol blends. At the low concentrations currently permissible, ethanol, methanol, n-propanol, isopropanol, and tert-butanol elevated the vapor pressure of a gasoline blend to greater than that of either of the components, although in pure form, the vapor pressures of all neat alcohols are less than those of gasoline. The other butanol/gasoline blends (n-butanol, sec-butanol, and isobutanol) do not show a vapor pressure increase at low alcohol concentrations (over the vapor pressure of gasoline alone), although their vapor pressure behavior is elevated above predictions based on ideal behavior.

Figure 7 shows the vapor pressure of various concentrations of methanol, ethanol, isopropanol, and tert-butanol with gasoline. The vapor pressure bump at low alcohol concentrations can be explained by the high polarity of alcohol molecules in comparison to the gasoline hydrocarbons. In neat solution, polar molecules are strongly attracted to each other and form hydrogen bonds between molecular extremities of opposite polarity. This reduces the vapor pressure for these molecules to levels below those that would normally be expected based on molecular size. However, when polar compounds are heavily diluted by the nonpolar molecules of gasoline, these bonds are no longer effective, and the polar molecules can more readily leave the solution and become gaseous. It is not surprising that the increase in volatility is less with less polar, higher molecular weight alcohols.

Blending a higher alcohol (which lowers the overall vapor pressure) into an ethanol/gasoline mixture can mitigate the vapor pressure increase as shown in Figure 8.

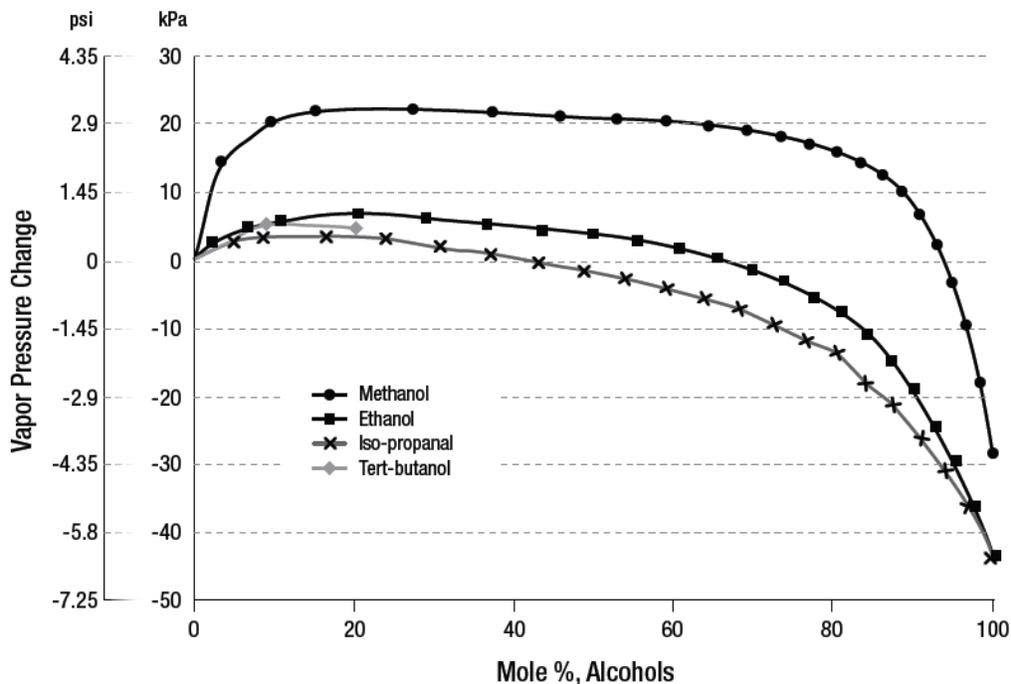


Figure 7. Vapor pressure of alcohol/gasoline blends<sup>79</sup>

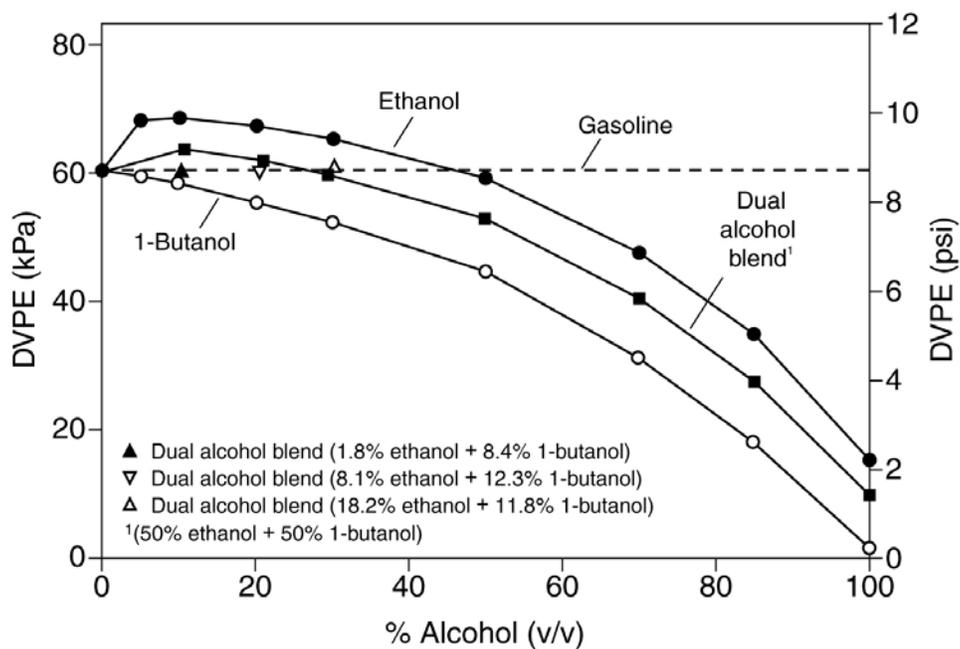
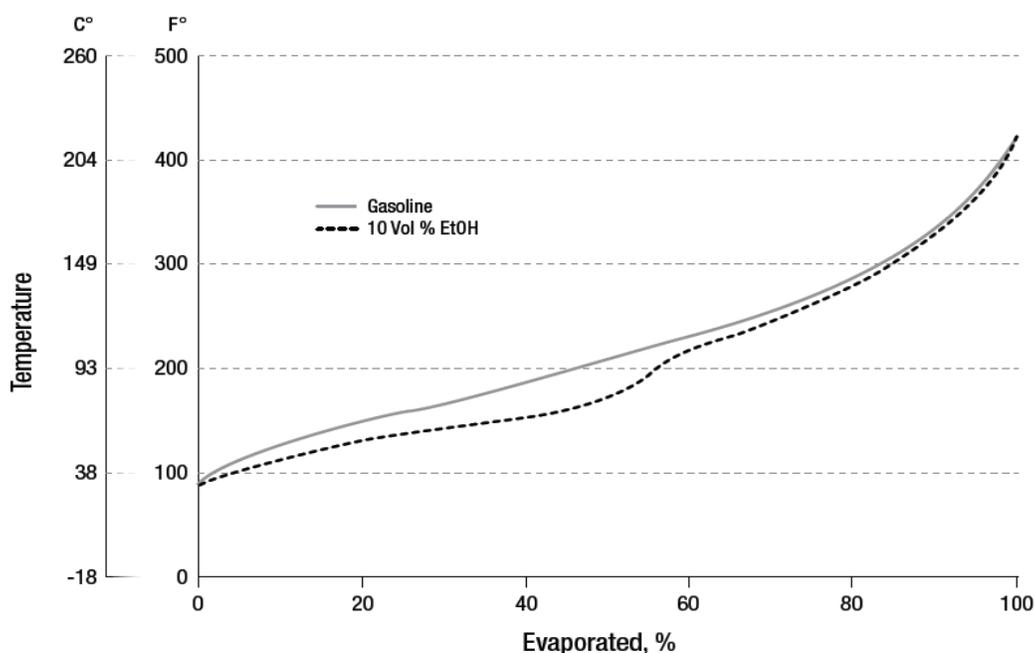


Figure 8. Vapor pressure (as Dry Vapor Pressure or DVPE) of ethanol and n-butanol in gasoline, added individually and in a dual alcohol blend.<sup>52</sup>

In addition, the use of alcohols (at least methanol and ethanol) in gasoline causes a depression of the midsection of the otherwise smooth gasoline distillation curve (see Figure 9). This has been associated with difficulty in cold starts. Andersen et al. have reported the distillation curves for alcohols up to n-butanol, including dual alcohol blends.<sup>80</sup> The higher alcohols have a lesser effect, and the flattening of the curve appears at higher temperatures, as would be expected. A distillation curve will have a flat section near the boiling point of any specific compound that is present at relatively high concentrations, and the higher alcohols boil at higher temperatures than ethanol and methanol. Using a higher alcohol in combination with methanol reduces the flattening of the curve near the methanol boiling point, but does not eliminate it.

To further complicate the issue, the vapor pressure and distillation curve of the base gasoline can be varied in the refining process. Starting with a gasoline that has a lower vapor pressure would result in a blend with a lower vapor pressure. To lower the vapor pressure in gasoline, refiners typically remove butanes.<sup>81</sup> However, excessive removal of butanes (some of the lowest boiling point components of gasoline) can adversely affect a vehicle's cold-start characteristics.<sup>44</sup>



**Figure 9. Distillation curve for 10 vol% ethanol/gasoline blend.**<sup>44</sup>

Evaporative emissions from vehicles and from fuel storage are roughly proportional to the volatility of the fuel blend, although such factors as elastomer deterioration and permeability and the loss of canister capacity in the presence of alcohol may increase evaporative losses of alcohol blends.<sup>82</sup> Quantifying and reducing permeation emissions of ethanol/gasoline blends from vehicles is an area of recent research, but there is little recent information regarding evaporative emissions of other oxygenates. In the early 1980s, Furey and King measured evaporative emissions from cars using two blends of equal amounts of methanol and butanol in gasoline. They found that the evaporative emissions were 41% to 44% higher with a 10% blend than with gasoline and 26% to 30% higher with an 18% blend. These results are consistent with the relative volatility of the fuels.<sup>82</sup> However, there have been dramatic changes in evaporative

emission control technology since the 1980s, so evaporative emission impacts for modern vehicles are likely to be significantly different.

### 7.3 Phase Separation

Water is virtually insoluble in gasoline and completely miscible with ethanol, methanol, tert-butanol, and GVL. The water solubility of most of the other higher alcohols and oxygenates falls somewhere in between these two extremes. When they are in contact with enough water, these somewhat soluble compounds will divide into two phases—a primarily aqueous phase that contains some oxygenate, and a primarily oxygenate phase that contains some water. This different behavior in relation to water affects the acceptable storage requirements of the various fuels. Alcohol and other water-soluble fuels should be kept dry, while gasoline can generally tolerate some contact with water because the water is not taken up and thus will not affect use of the gasoline. (Note that “water tolerance” as specified in D4814-10 is measured as the temperature at which phase separation occurs. This will depend on the amount of water in the blend and the oxygenate concentration.)

Some have argued that phase separation in the presence of water is the most serious technical problem associated with ethanol/gasoline blends.<sup>83</sup> Water solubility in gasoline is very low and thus not a significant performance concern. If water gets into the gasoline transport system, it typically pools at the bottom of storage tanks or pipes. However, even small amounts of ethanol significantly increase the solubility of water in the hydrocarbon phase. The higher dissolved water content can reduce the energy density of the fuel, but more important, if sufficient water is encountered, a separate aqueous phase will extract ethanol out of the gasoline. The separate aqueous phase can form as the gasoline is cooled in cold weather or if an ethanol/gasoline blend is mixed with a fuel having a different ethanol content. ASTM D4814-08b requires that gasoline alcohol blends be kept dry enough that they do not separate into a water/alcohol phase and a hydrocarbon phase down to the lowest temperatures they are likely to encounter.

The loss of ethanol into a separate water phase can reduce the octane to below acceptable limits, and if the separate phase occurs in the engine, it can cause significant driveability problems. In addition, some believe that the water in the fuel, which as conditions change could come out of solution, can increase the corrosiveness of the blend.

The solubility of water in a gasoline/oxygenate blend is highly dependent on the type of oxygenate. The amount of water that can be dissolved in various 10% and 20% alcohol blends in gasoline is shown in Figure 10. It is interesting to note that the solubility of water in the blends increases in the following order: methanol, n-butanol, ethanol; the most water dissolves in the n-propanol/gasoline blend, suggesting that, for the purposes of reducing water-related problems, n-propanol should be avoided as an additive to gasoline. In contrast, n-butanol should provide a significant benefit over ethanol. Gasoline/n-butanol blends can avoid phase separation to significantly lower temperatures than can gasoline/ethanol blends having equivalent oxygen content. Other testing by the same team of researchers, using n-heptane as a surrogate for gasoline, supports these relative solubility rankings and showed decreasing solubility for water in the organic phase as the chain length increased to C<sub>4</sub> and above (see Table 8).<sup>84</sup>

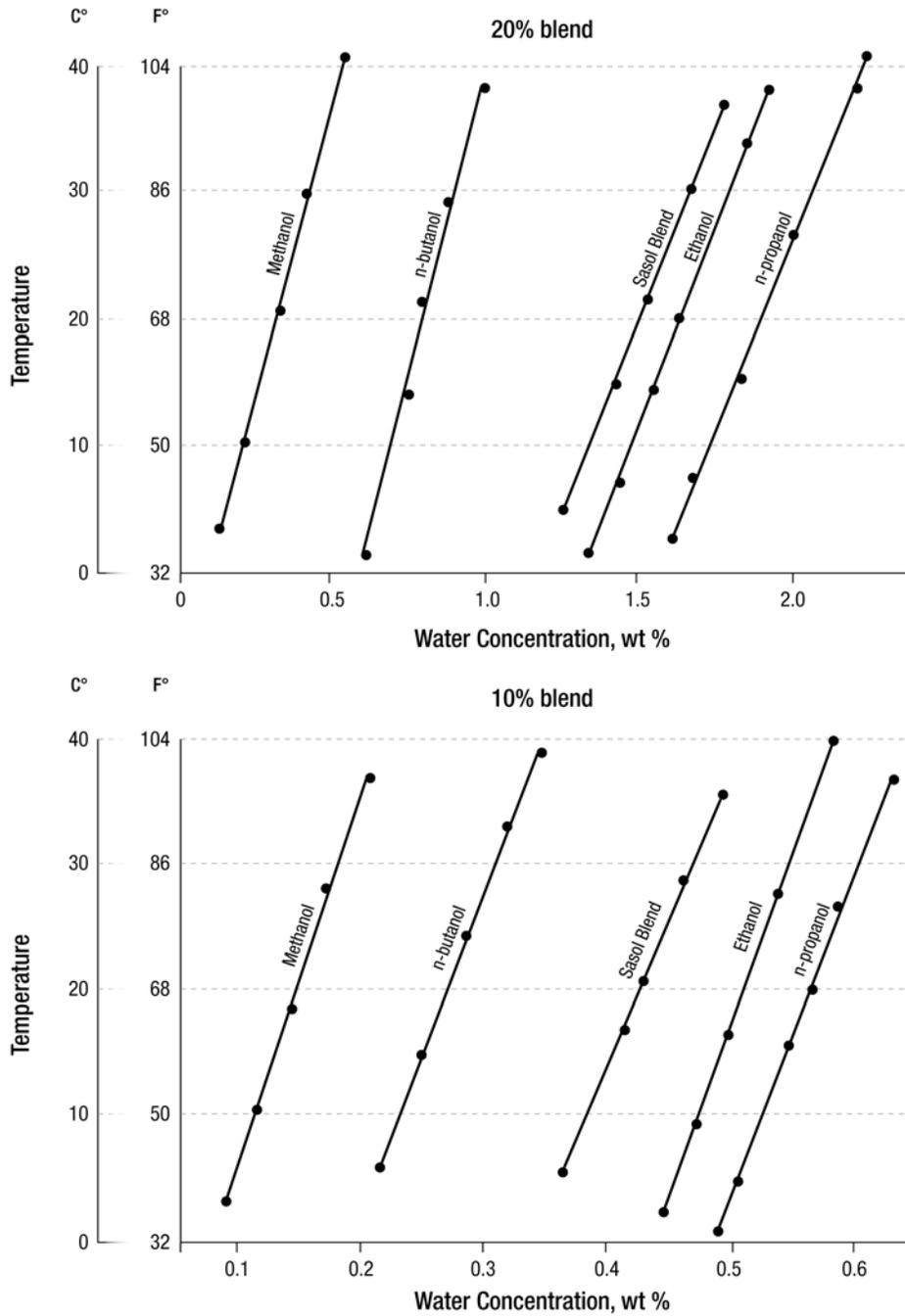
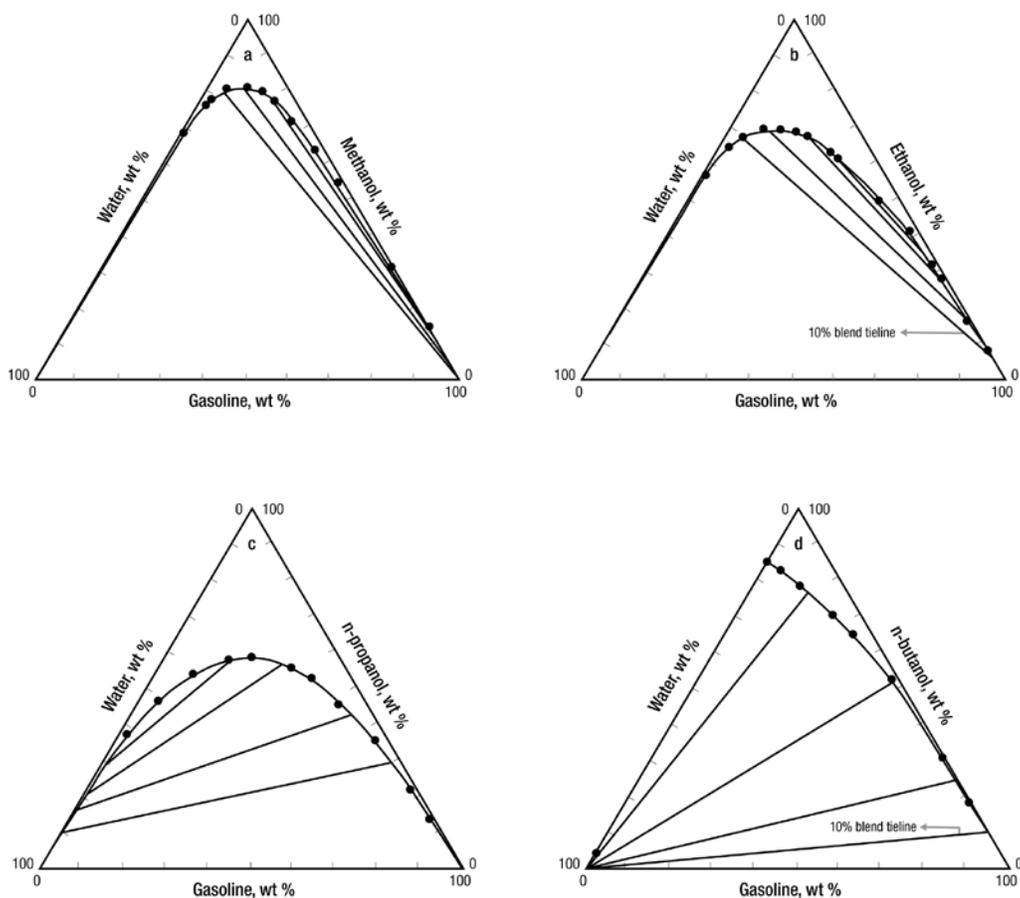


Figure 10. Solubility of water in 10 wt% and 20 wt% mixtures of various alcohols in gasoline<sup>85</sup>

Table 8 also shows the mole fraction of water in the corresponding aqueous phase, in the right-hand column. The 1.00 values at the bottom of this column show that the fairly nonpolar higher alcohols will remain for the most part in the gasoline. In contrast, methanol and ethanol will largely partition out of the gasoline phase into the aqueous phase. This is also shown graphically as ternary phase diagrams in Figure 11. In this figure, the curve passing through the data is the binodal curve and the lines shown are the tie-lines. The single-phase region is the area outside or above the binodal curve. A point inside (below) the binodal curve will not exist in equilibrium; it represents a composition of gasoline, water, and alcohol that will separate into two separate phases, a water-rich phase and a gasoline-rich phase. At either end of a tie-line are the composition points of the two coexisting phases. The tie-lines connect the composition points on the binodal curve of the water-rich and gasoline-rich phases that form for the ternary compositions along the tie-line. The methanol and ethanol tie-lines slope down to the right precipitously, indicating that these alcohols will partition quite strongly into the water phase (the water phase contains a much higher level of alcohol than the gasoline phase). In contrast, with their left-leaning tie-lines, n-propanol and (even more strongly) n-butanol will preferentially partition into the gasoline phase. In all cases, the addition of even small amounts of water to a 10% alcohol in gasoline blend results in phase separation.

**Table 8. Mole Fraction of Water in the Organic Phase and Aqueous Phases When Combined with 15% Alcohol/n-Heptane Blend<sup>84</sup>**

<b>Alcohol Component</b>	<b>Water Mole Fraction in Organic Phase</b>	<b>Water Mole Fraction in Aqueous Phase</b>
Methanol	0.000	0.04
Ethanol	0.016	0.55
n-Propanol	0.023	0.84
Isopropanol	0.025	0.85
n-Butanol	0.009	0.99
sec-Butanol	0.012	0.98
tert-Butanol	0.014	0.99
n-Pentanol	0.012	1.00
2-Pentanol	0.012	1.00
n-Hexanol	0.005	1.00



**Figure 11. Binodal curves and tie-lines for gasoline-water-alcohol ternary liquid systems.<sup>85</sup>  
See footnote for explanation of ternary phase diagrams.\***

To understand what this means in practice for the different alcohols, consider, for example, a 20% n-butanol/gasoline blend that is fully saturated with 0.8% water at 20°C (see Figure 11). If that mixture is combined with an equal amount of pure gasoline, however, the 10% blend that results can hold only about 0.25% water (much less than half), and the extra water would drop out of solution and form a separate aqueous phase. Because the n-butanol will partition preferentially into the gasoline phase (see the marked tie-lines in Figure 11), virtually all of the

\* In an ordinary x-y graph all the isoconcentration (constant concentration) lines for one constituent run parallel to each other, and perpendicular to those of the other constituent. In a ternary graph, the isoconcentration lines for each constituent are still parallel to each other, but at a 60° angle to those of the other constituents. By convention, the isoconcentration lines for each constituent run parallel to the axis to the left. Thus, in these graphs, a horizontal line represents a constant concentration of alcohol. Isoconcentration lines for water slope down to the right parallel to the alcohol axis and gasoline isoconcentration lines slope upward to the right parallel to the water axis. For example, for gasoline, the 50% concentration line slopes upward to the right from the middle of the bottom axis at the point representing 50% gasoline, 50% water and 0% alcohol, to end on the alcohol axis at the point representing 50% gasoline, 0% water and 50% alcohol. In these graphs the isoconcentration lines are implied; the drawn lines are tie-lines, which are explained in the text.

n-butanol will remain in the gasoline, and the gasoline/butanol product will remain usable. The separate water phase will have very low concentrations of n-butanol. If the alcohol used had instead been ethanol, the concentration of water in the 20% ethanol/gasoline blend could have been as much as 1.6%. This higher concentration of water will present more operability problems if it comes out of solution in the fuel tank (perhaps because of the dilution of the ethanol concentration by gasoline or because of a temperature drop). If there is a significant amount of water, the loss of ethanol to the aqueous phase could reduce the octane level of the gasoline phase to below acceptable levels, and if phase separation occurs in the transportation system, the fuel value of the ethanol can be lost.

In Figures 10 and 11, the Sasol company's blend seems to act somewhere near the average of its various ingredients, suggesting that there is little synergistic effect between the various alcohol ingredients. However, others have reported that butanol can be used as an additive to increase the solubility of ethanol in gasoline to avoid phase separation.<sup>82</sup> This is an important issue that should be resolved with additional testing.

Little is known about the partitioning behavior of other oxygenates, although DMF, MF, and MP have very low solubility in water.

#### **7.4 Materials Compatibility**

Information on the materials compatibility of various pure alcohols with fuel storage and handling components can be qualitatively compared with gasoline on the basis of chemical compatibility charts available from numerous equipment suppliers.<sup>86,87</sup> In these charts, alcohols are considered slightly more corrosive than gasoline when they are in contact with some of the most commonly used metals (aluminum, brass, carbon steel, stainless steel), i.e., they receive a "good" rating as opposed to an "excellent" rating. Cast iron should not be used in alcohol service, although it is acceptable for gasoline. Higher alcohols are expected to be less aggressive than the shorter chain alcohols.<sup>88</sup> Most plastics and elastomers are approved for use with alcohols, with the exception of the use of some grades of Viton with methanol or ethanol; polyurethane and polyacrylates are also not recommended for use with alcohols. The use of zinc, brass, lead, and aluminum is not recommended with E85<sup>89</sup> and could also be an issue with pure ethanol or other neat fuels.

Despite the guidance from equipment manufacturers regarding carbon steel, in practice stress corrosion cracking has proven to be an issue in carbon steels in contact with denatured fuel-grade ethanol in some situations.<sup>90</sup> While the reason for this disparity between equipment manufacturer guidance for neat alcohols and the practical experience of ethanol fuel users is not fully understood, it is an area of significant current research, especially in regard to shipping ethanol in steel pipelines. Some theorize that ethanol has proven to be more corrosive in fuel use because of the presence of dissolved oxygen.<sup>88</sup> Others believe that corrosion issues may be aggravated by high levels of water in the fuel.<sup>84</sup> The extent to which this issue applies to higher alcohols and other oxygenates is unknown.

As discussed earlier, pure higher alcohols are generally less reactive with most materials than are shorter chain alcohols. However, it is not clear how to extrapolate this information to blends, because in some cases, materials that are compatible with both neat gasoline and neat ethanol are

incompatible with ethanol/gasoline blends.<sup>83,91</sup> In addition, there is the question of whether there are synergistic effects between different alcohols combined in gasoline.

Although it is known that neat methanol greatly increases engine wear rates, tests conducted on older vehicles indicate that alcohol blends of up to 4.5% methanol/4.5% gasoline-grade t-butyl alcohol (GTBA) and 16% GTBA blends do not cause increased engine wear or deposits over that for normal hydrocarbon gasoline.<sup>92</sup> (A 1981 EPA waiver allows the use of tert-butanol combined with additional high-volatility butanes, a blend known as GTBA.)

BP has conducted extensive trials using 11.5% to 16% butanol blends in gasoline on vehicles up to 10 years old in the United Kingdom and found no material compatibility issues. They specifically compared butanol/gasoline blend compatibility with aluminum components with ethanol/gasoline blends and found no corrosion at all with butanol/gasoline blends. Corrosion was found when ethanol/gasoline blends were used.<sup>8</sup>

In Japan, Kameoka et al.<sup>93</sup> examined the corrosive impacts of relatively high concentrations (35% to 100%) of alcohols, including ethanol, n-propanol, isopropanol, n-butanol, and isobutanol in gasoline on various metals. Aluminum was considerably corroded at all alcohol concentrations tested, while steel and nickel were relatively unaffected. Copper was also visibly damaged by the alcohol blends. Tin and zinc were less consistently affected. Alcohols with fewer carbon atoms and with straight chains, as opposed to higher alcohols and branched alcohols, tended to be more corrosive, suggesting that ethanol blends represent a worst case.

Lange et al.<sup>31</sup> have compared the elastomer swell caused by ethanol with that caused by EP and EL. Although specific experimental methods were not detailed, they found that EP had the smallest effect on the tested elastomer, and EL was the worst.

## **7.5 Driveability**

Driveability is a measure of the smoothness of engine performance and will differ with different fuels. A methodology has been developed using trained, experienced drivers and a rating system that ranges from 1 (vehicle not operating) to 10 (not noticeable by an experienced driver) to compare the performance of different engines over a range of vehicle operating situations. BP has measured driveability performance for a range of butanol/gasoline blends and found that, while driveability performance tends to degrade at higher concentrations, driveability performance is indistinguishable from the gasoline over a broad range of butanol concentrations.<sup>8</sup> [Note that the “Driveability Index (DI)” in ASTM D4814 is intended to be a surrogate for driveability, but is based on the distillation curve. It has been specifically modified for ethanol, but has no correction factor for other oxygenates.]

## **7.6 Octane Rating**

Ideally, fuel is ignited at a precise time in the piston's stroke cycle and propagates as a uniform flame front, but in some cases, pockets of fuel ignite outside the envelope of the normal combustion flame front. The shock waves created by this ignition event result in a characteristic metallic “knocking” sound and can result in power loss or engine damage in very severe cases. Certain fuels and additives are less prone to knock. The resistance of a fuel to knock is expressed as its octane number.

There are two ways to measure octane number. The research octane number (RON) is measured by running the fuel in a test engine with a variable compression ratio and comparing its knock resistance to a known fuel standard. The motor octane number (MON) is a similar measurement made under conditions that further stress the fuel's knock resistance, including a higher engine speed, variable ignition timing, and a preheated fuel. Typical fuel specifications require a minimum value for both RON and MON. For conciseness, the knock resistance is often given as the anti-knock index (AKI), which is the average of the RON and the MON. In addition, for low-concentration additives, one can calculate a blending octane number, assuming that the additive raises the blend octane in proportion to its volumetric concentration. In some cases, these blending octane numbers can differ from the pure component octane number, but generally there is a rough correlation.

Octane values can be higher than those required for a specific engine although the higher level provides no additional benefit. Thus, the octane levels of neat methanol, ethanol, n-propanol, n-butanol, isobutanol, tert-butanol, and isopentanol as well as all of the other oxygenates considered here, with the exception of MTHF, are appropriate for most on-road spark-ignition engines (see Tables 5 and 6). N-pentanol also has a relatively low blending octane number. Interestingly, recent testing of DMF in a single cylinder direct-injection research engine found engine knock occurring at loads similar to gasoline and much lower than ethanol, which is surprising given the high octane level reported in the literature.<sup>55</sup>

Engines designed for higher octane fuels operate at a higher compression ratio, which makes them more efficient and allows them to provide more power with the same volume combustion chamber. For example, Saab's 2.0-liter turbocharged, four-cylinder engine has an 11.0:1 compression ratio when optimized for ethanol, compared with 8.8:1 for a similar-sized gasoline engine. Saab claims that this allows its 2.0-liter engine to provide the power of an equivalent 4.0-liter engine running on gasoline. Saab's goal was a more powerful engine. Popuri and Bata<sup>49</sup> used the same concept to make a more fuel-efficient engine. They found that the brake-specific fuel consumption of isobutanol blends could be as good as, or better than, that of gasoline if the compression ratio of their single-cylinder research engine was adjusted to account for the higher anti-knock qualities of the alcohol additives.<sup>49</sup> Note that, for commercial engines on the road today, the compression ratio is fixed by the engine design and cannot be adjusted for different fuels.

When fuels having different octane numbers are blended, the octane number of the blend cannot be calculated linearly. Rather, it must be measured, and then a "blending" octane number can be calculated that gives a rough estimate of the octane effect that an additive has on the total blend. Ethanol, methanol, and tert-butanol all have blending octane numbers that will increase the octane number of typical gasoline. However, for many of these compounds, blending octane values are not available in the scientific literature. Measurement of the blending octane numbers for those oxygenates for which the value is not yet known is a relatively inexpensive and worthy research goal.

## **7.7 Heat of Vaporization**

Neat alcohols and alcohols combined with gasoline at high concentrations have a higher heat of vaporization than gasoline does. Of the non-alcohol oxygenates, the heat of vaporization is only

known for a few of the compounds. Except for the relatively high heat of vaporization of GVL, the others are comparable to gasoline and thus would not be expected to significantly impact engine operation. If the heat of vaporization is high, the increased evaporative cooling effect can change combustion characteristics and lower the intake charge temperature and hence increase the intake air density. Since a greater mass of air can be injected at the lower temperature, the corresponding fueling rate can also be higher, yielding more power from an engine of the same size. Alternatively, a higher heat of vaporization can make it more difficult to evaporate fuel in cold conditions, leading to more cold start issues.

## 7.8 Tailpipe Emissions

Gautam et al. tested emissions from various blends of alcohols at 10% total concentration in gasoline in a single-cylinder research engine.<sup>94</sup> Each blend included methanol, ethanol, propanol, butanol, and pentanol, but in different proportions, while keeping the total oxygenate concentration at less than 3.7% and the total methanol concentration at less than 5%, so that these blends could legally meet the requirements for the DuPont waiver mentioned in Table 2. The compression ratio of the engine was adjusted to maximize engine efficiency, and despite the slightly lower energy density of the alcohol blends, the engine used about 20% less mass of alcohol fuel on a delivered-power basis. This is because the higher octane of the fuel combination allowed for a higher compression ratio. Emissions of CO were 16%–20% lower, emissions of carbon dioxide were 18%–23% lower, emissions of NO<sub>x</sub> were 5%–11% lower, and emissions of organic materials-hydrocarbon equivalent was reduced 17%–23 % on a brake-specific basis. On a fuel-specific basis, emissions were about the same, except that NO<sub>x</sub> showed a slight increase. In recent testing, BP measured emissions on 16% butanol in gasoline blends for in-use cars and found no significant change in emissions of CO or NO<sub>x</sub> and a slight reduction in hydrocarbon emissions.<sup>8</sup>

In 1988, Furey and King tested the addition of a 2:1 mixture of methanol and butyl alcohols at concentrations of 10% and 18% in four cars—one with an open-loop system and three with closed-loop systems.<sup>82</sup> They found that the alcohol mixture reduced CO at all concentrations in all four cars by 20% to 50%, as a result of the leaning effect of the alcohol. For NO<sub>x</sub> and hydrocarbons (HC), the results were mixed with no consistent trend, and differences in HC emissions between the alcohol blends and pure gasoline were consistently small (less than 7% in all cases).

Namun and Allsup<sup>95</sup> tested pre-Tier 1 closed-loop control vehicles on the Federal Test Procedure. The addition of 7% tert-butanol to the base fuel decreased fuel economy by 4.3% and HC and CO emissions by 26% and 22%, respectively; NO<sub>x</sub> and evaporative emissions increased by 21% and 5%, respectively. When compared with the base fuel, the exhaust aldehydes were 2.3 times higher with the tert-butanol blend. In contrast, the addition of 10% ethanol to the base fuel decreased fuel economy by 2.7%, decreased HC emissions by 9%, decreased CO emissions by 27% and increased NO<sub>x</sub>, and evaporative emissions by 23% and 15%, respectively.

While it is premature to draw firm conclusions on the limited testing done to date, the most recent data suggest that low concentrations of higher alcohols will have only a small, potentially positive impact on regulated emissions from cars. Specifically, emissions testing of the most modern Tier 2 vehicles using higher alcohol fuels is very limited, and more testing of these

vehicles especially is warranted. Testing will need to include the impact of alcohols on emission control system durability. In addition, the potential for toxic emissions from the partial combustion of higher alcohols may be of significant concern. Aldehydes are known to form in the emissions from alcohol-fueled cars. For higher alcohols, emitted oxygenates could include unburned alcohols and potentially a range of aldehydes and ketones with carbon numbers from C<sub>1</sub> up to that of the highest carbon number alcohol in the fuel. In calculating NMOG, many laboratories measure only ethanol, formaldehyde, and acetaldehyde today, although the carbonyl analysis procedures are easily extended to higher molecular weight materials. Less is known about the quantification of unburned higher alcohol in vehicle exhaust.

Emissions tests have been conducted on a 60% MTHF/40% gasoline blend in a 1990 Dodge Dynasty closed-loop engine and compared to straight gasoline.<sup>96</sup> The results showed a large reduction in HC and NMOG (by about 52%, average of three tests), small but significant reductions in CO (20%, average of three tests) and a statistically insignificant increase in NO<sub>x</sub>. Formaldehyde and acetaldehydes increased by 53% and 87%, respectively, and benzene was reduced by 73%. 1,3-Butadiene results were ambiguous. Fuel economy was reduced about 7%.

DMF has also been tested as a neat fuel in a direct injection research engine.<sup>55</sup> Emissions of CO, HC, and NO<sub>x</sub> were intermediate between those of neat ethanol and those of neat gasoline.

For all of the new oxygenate compounds, it is critical to identify any toxic compounds in the emissions, and speciation of engine exhaust should be an important future research goal.

There are few data on evaporative emissions effects, which in modern cars could represent up to 50% of all emissions. While higher alcohols and the other oxygenate compounds will have a significantly lower vapor pressure impact than ethanol does, it is not known how these alcohols will affect the permeation of fuel through fuel system elastomeric components. Detailed studies of evaporative emissions from Tier 2 vehicles are therefore required.

## **7.9 Viscosity**

The higher alcohols have a significantly higher viscosity than both gasoline and ethanol (see Table 5). The viscosity of isobutanol is significantly higher than that of the other alcohols evaluated. If higher alcohol blends with gasoline also have higher viscosities, this might stress the fuel pump or change spray pattern characteristics. Viscosity measurements of blends would be a worthy research goal that could explain the cause of emissions and operational changes with the addition of higher alcohols. Note also that tert-butanol is a solid at room temperature and thus impossible to pump except at elevated temperatures. Viscosity impacts of the other oxygenates will also need to be evaluated in the future.

## **7.10 Impurities**

The presence of impurities such as lead, sulfur, and gums will depend on the feedstock and the method used to produce and purify these compounds. However, both fermentation and synthesis via synthesis gas can produce alcohols that are very low in these impurities, although contaminated feedstocks could change that situation. Sulfur is a significant concern, as allowable sulfur levels in spark-ignition fuels are very low. A detailed assessment of impurities in fuel blends is needed for each viable production method along with emission control system durability studies of the effects of impurities not already considered in current regulations.

## 8 CONCLUSIONS AND RESEARCH NEEDS

A range of different gasoline boiling-range oxygenates can be produced from ligno-cellulosic biomass using either biochemical or thermochemical means. This report has reviewed the properties of these materials and the published literature on their performance in spark-ignited engines.

All gasoline oxygenate blends must meet the most recent version of ASTM Standard D4814 if they are to be treated as conventional gasoline, which includes a number of fundamental functional requirements related to volatility, oxidation stability, corrosiveness, octane number, impurity levels, and other properties. In addition, there are requirements against phase separation that will depend upon the quantity of water absorbed by the fuel. With the exception of GVL, the propanol isomers and tert-butanol, the amount of water taken up by blends of the studied oxygenates with gasoline is expected to be less than for ethanol blends and thus expected to be less problematic. Very little data exist on how blending of these compounds with gasoline or unfinished gasoline (blendstock for oxygenate blending) affects the D4814 properties, especially the vapor pressure of the non-alcohol oxygenate/gasoline blends. Furthermore, the DI is not defined for oxygenate/gasoline blends other than ethanol, and the impact of these blends on driveability should be assessed. While material compatibility is also anticipated to be less an issue for higher alcohols and for most of the oxygenates that have a polarity less than ethanol, materials compatibility testing of all blends seems a reasonable step to take before their widespread use.

Little is known about by-products and minor contaminants that could be present in oxygenates from the various production processes. For these compounds to become widely used in gasoline blending, it is likely that certain impurities will have to be limited to protect engine and emission control components. Thus, it is likely that an ASTM specification for blending components, similar to the ASTM D4806 specification for fuel-grade ethanol, will have to be developed. The development of an ASTM specification will require a substantial amount of data on the chemical composition and properties of the alcohol of interest as well as on how impurities impact engine and emission control system durability.

Testing to obtain UL listing of dispensers and of both aboveground and underground storage tanks for use with oxygenates is required for widespread commercialization. This process will require evaluation of the compatibility of these compounds fuel blends with a range of elastomers, metals and plastics, as well as other testing to be defined by UL.

Limited emissions testing performed on pre-Tier 1 vehicles or research engines suggests that higher alcohols and MTHF will reduce emissions of CO and organics, while NO<sub>x</sub> emissions stay the same or increase. DMF is also shown to have a small, but beneficial effect on CO, organics, and NO<sub>x</sub> emissions. It is not clear that these effects would be observed in Tier 2 vehicles with modern emission controls. Also, there is no public information on the impact of higher alcohols and oxygenates on emissions of specific toxic compounds. This is a critical research need. Methods for measuring the oxygenate fraction of NMOG will have to include carbonyl compounds of higher molecular weight than acetaldehyde, other oxygenate combustion products, as well as unburned oxygenate. The impact of higher alcohols and oxygenates on evaporative

emissions, including permeation effects, has not been studied. The impact of these alcohols on the durability of emission control catalysts must also be investigated. Similar research will have to be completed for other oxygenates.

The high toxicity of DMF and MF suggests that special care must be taken in assessing emissions to ensure their use would not present an exceptional risk, although tailpipe emissions speciation is needed prior to the use of any gasoline additive. Safety issues associated with the formation of peroxides in MTHF will also need to be assessed.

The millions of FFVs currently on the road are designed to run on ethanol concentrations of up to 85%. These vehicles may also be capable of running on high-percentage blends of higher alcohols and oxygenates. The compounds considered here have a higher energy density than ethanol, so compensation for energy density will be less of an issue. However, the vapor pressure of higher alcohols and the oxygenates is in most cases lower than that of ethanol; thus, cold startup might be a problem, and higher gasoline content relative to E85 might be required for cold weather operation. Advanced vehicles, with preheaters for cold starts and engines capable of optimizing calibration for a wide range of fuel energy densities, are feasible with current technology but do not exist in significant numbers in the commercial marketplace today.

In the longer term, the performance of higher alcohols and other oxygenates in advanced engines employing direct injection or low-temperature combustion strategies should be investigated

Fuel use of GVL will be held back by its potential for abuse as a drug. Although ethanol also has the potential for abuse and addiction, its widespread availability elsewhere minimizes the potential for additional disruption caused by fuel use. Additionally, GVL's miscibility with water and its high boiling point (and presumably low vapor pressure at typical ambient temperatures) present significant drawbacks to its use as a gasoline substitute or additive. The same can be said for tert-butanol, which is also miscible with water. Moreover, no pathway for the production of tert-butanol from renewable sources has yet been proposed.

For ML and EL, based on the limited information available on phase change temperatures, there is some evidence that these compounds will be not volatile enough to be used in existing vehicles. The solubility of ML and EL in gasoline should be measured, as well as the volatility of low concentration levulinate/gasoline blends as a next step in assessing the utility of these compounds as gasoline extenders.

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