

Selection Criteria and Screening of Potential Biomass-Derived Streams as Fuel Blendstocks for Advanced Spark-Ignition Engines

Robert L. McCormick, Gina Fioroni, Lisa Fouts, and Earl Christensen
National Renewable Energy Laboratory

Janet Yanowitz
Ecoengineering Inc.

Evgueni Polikarpov, Karl Albrecht, and Daniel J. Gaspar
Pacific Northwest National Laboratory

John Gladden and Anthe George
Sandia National Laboratory

Abstract

We describe a study to identify potential biofuels that enable advanced spark ignition (SI) engine efficiency strategies to be pursued more aggressively. A list of potential biomass-derived blendstocks was developed. An online database of properties and characteristics of these bioblendstocks was created and populated. Fuel properties were determined by measurement, model prediction, or literature review. Screening criteria were developed to determine if a bioblendstock met the requirements for advanced SI engines. Criteria included melting point (or cloud point) $< -10^{\circ}\text{C}$ and boiling point (or T90) $< 165^{\circ}\text{C}$. Compounds insoluble or poorly soluble in hydrocarbon were eliminated from consideration, as were those known to cause corrosion (carboxylic acids or high acid number mixtures) and those with hazard classification as known or suspected carcinogens or reproductive toxins. Compounds predicted to be less anaerobically biodegradable than methyl-tert-butyl ether with water solubility greater than 10,000 mg/L were also eliminated. A minimum Research octane number (RON) of 98 was applied. These criteria produced a list of 40 bioblendstocks with promising properties. Additional property data, including Motor octane number (MON), heat of vaporization, and lower heating value, were acquired for these bioblendstocks. A subset of the bioblendstocks representing all functional groups were blended into gasoline or a gasoline surrogate to measure their effect on vapor pressure, distillation curve, oxidation stability, RON, and MON. For blending into a conventional or reformulated blendstock for E10 blending, ethanol, 2-butanol, isobutanol, and diisobutylene have the most desirable properties for blending of a high-octane advanced SI engine fuel.

Introduction

Reducing greenhouse gas emissions from the light-duty transportation sector will require both low-net-carbon fuels and significant improvements in vehicle and engine efficiencies. The U.S. Department of Energy's Co-Optimization of Fuels and Engines (Co-Optima) program is developing the scientific and technical foundation to co-optimize fuels and engine architectures, designed in tandem to maximize performance and carbon efficiency. The initial focus is on the science and technology for improving performance, efficiency, and emissions of spark ignition (SI) engines. Advanced SI engines employ technologies that lead to reduced energy use, such as higher compression ratio, and higher power density, turbocharged

engines that enable smaller swept displacement volume (downsizing) and operation at lower engine speeds (downspeeding) [1-6]. Engines utilizing these technologies require fuel with significantly higher knock resistance than is commonly available today.

In this work a list of potential bioblendstocks, including those that can be produced biochemically or chemically or by hybrid processes, was developed based on input from the biofuel production research community. We also developed a tiered screening framework for categorization and screening of proposed bioblendstocks based on fuel properties. A methodology for determining fuel properties by measurement, model prediction, or literature review was created. The data were used to populate a publicly accessible online database [7]. Using this information, potential blendstocks were screened for their suitability as advanced SI engine fuel components based on the measured or predicted blendstock properties. This led to a list of bioblendstocks with the desirable properties, whose predicted properties were then confirmed by measurement, and additional property data were also obtained. The goal of this research is to develop bioblendstocks that would be blended into petroleum-derived basestocks at up to about 30 percent by volume (vol%). Accordingly, blends in gasoline of bioblendstocks with promising properties were prepared, and key blend properties were measured.

Bioblendstock Categorization and Screening Approach

A three-tiered fuel screening approach was developed. Tier 1 screening determines if a blendstock can, in the first instance, be used as a fuel, and if so, whether it is likely to have desirable fuel properties for advanced SI engines. Tier 1 criteria include physical properties such as boiling point, melting point, solubility, basic safety criteria such as toxicity, peroxide forming potential, and corrosivity. Research octane number (RON) was used as the autoignition metric. These criteria are shown in Table 1 with the rationale for the choice of each property. The approach for applying these metrics for Tier 1 screening is shown in Figure 1. Blendstocks falling outside the defined ranges for these properties were excluded.

Other metrics were also considered for Tier 1. Rejection of fuels that are highly water soluble was considered but not included because water-soluble blendstocks (ethanol) have been successfully introduced into the market (although water solubility is relevant to

anaerobic biodegradability as discussed below). Similarly, lower heating value was considered but rejected because of the success of ethanol, with a much lower energy density than gasoline, in the market.

Table 1. Tier 1 evaluation criteria for nominally pure compounds and mixtures.

Property	Purpose
Nominally pure compounds	
IUPAC name & synonyms; CAS#	Unambiguous identification of blendstock and basic properties for a range of calculations and measurements
Molecular weight	
Molecular formula	
Boiling point	Categorization as gasoline-like or diesel-like
Melting point	Blendstock handling in terminal environment
Solubility in hydrocarbon	Based on solubility parameter theory
OSHA Hazard Classification	Known human carcinogens or teratogens will not be allowed in fuel per OSHA regulations
Peroxide former	Safety in handling
Corrosion metric	Blendstocks that are too corrosive to metals will not be considered
Autoignition metric (RON)	Critical metric for determining if acceptable for advanced SI engines
Biodegradation	Screening of anaerobic biodegradation and water solubility
Mixtures	
Carbon, hydrogen, nitrogen, and sulfur content	Identity of blendstock and basic property for a range of calculations and experiments
Distillation curve	Categorization as gasoline-like or diesel-like
Cloud point	Blendstock handling in terminal environment
Solubility in hydrocarbon	Approximate determination of hydrocarbon solubility
Toxicity	Known human carcinogens or teratogens will not be allowed in fuel per OSHA regulations
Peroxide former	Safety in handling
Corrosion metric	Blendstocks that are too corrosive to metals will not be considered
Autoignition metric (RON)	Critical metric for determining if acceptable for advanced SI engines
Biodegradation	Screening of anaerobic biodegradation and water solubility

Tier 2 level screening includes metrics such as vapor pressure, distillation, oxidation stability, octane sensitivity, and blending octane – all measured for finished fuel blends. Tier 3 involves detailed engine combustion research and is not discussed here. In this paper no metrics related to economics, life-cycle sustainability, or market transformation issues are considered; however, these attributes are being assessed in subsequent tasks in the program.

Methods

Lists of potential biofuel blendstocks were developed based on literature reports and ongoing research at the national laboratories and at other organizations. Values for the Tier 1 properties listed in Table 1 were obtained from the literature, by direct measurement, or by estimation (as described below). The approaches taken for each property, and in some cases how that property was used to flag, categorize, or reject proposed blendstocks, are described in this section. The blendstock identity, composition, and properties were entered into a Filemaker database accessible to all [7]; therefore, not all blendstock properties are reported in this paper. At the time of this screening, the database included 369 nominally pure component blendstocks, 15 mixtures (including complex mixtures such as might be produced by catalytic fast pyrolysis, for example), and 115 finished fuel blends.

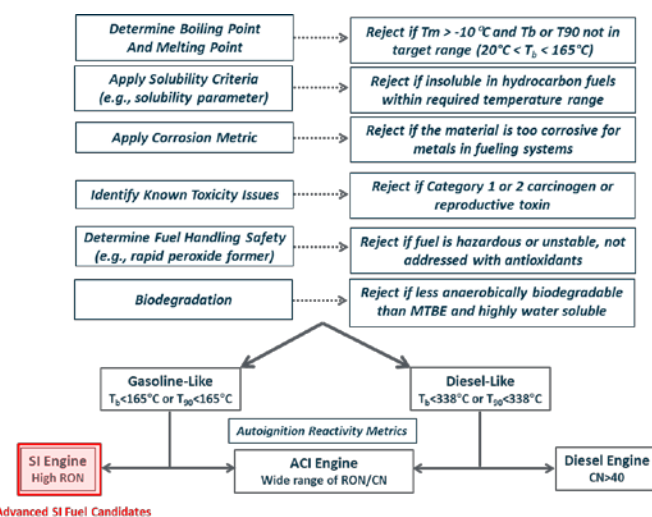


Figure 1. Decision framework for application of Tier 1 metrics for blendstock screening and categorization.

Boiling Point and Melting Point Values

Melting point (T_m) was used to screen for compounds with $T_m < -10^\circ\text{C}$ to ensure the blendstock could be handled and blended in a terminal environment. Boiling point (T_b) was used to first screen out compounds that were gases (requiring $T_b > 20^\circ\text{C}$), and second to select compounds boiling below (or mixtures having T90 below) 165° . The gasoline T90 limit is 185°C or 190°C ; however, for a gasoline blendstock near the T90 limit compounds that boil near the T90 limit cannot be blended at a significant volume percent without the finished blend exceeding the T90 limit.

Pure compound boiling and melting point data were acquired using SciFinder. If a measured value was not available, it was predicted using the publicly available program EPI Suite™ (accessed at chemspider.com). For mixtures (hydroprocessed pyrolysis oil, for example), distillation curves were provided by national laboratory researchers. These were typically measured by physical distillation using ASTM D86 or by simulated distillation using a gas chromatography method (ASTM D7096 – note the results obtained

by this method are similar to those measured by cryogenic, true boiling point distillation but may not be identical to D86 values). In some cases, a distilled gasoline boiling range material was not available, and we assumed that process conditions could be adjusted to produce a product meeting the T90 limit.

Prediction of Hydrocarbon Solubility

Because the anticipated use of the bioblendstocks is in a blend with petroleum-derived hydrocarbons, solubility in hydrocarbon is a critical parameter and was estimated using solubility parameter theory. The solubility parameter approach is widely used to predict chemical compatibility of fluids and elastomers. As developed by Hansen, the method includes three different parameters (Hansen solubility parameters) for dispersion (dD), polarity (dP), and hydrogen bonding (dH) [8].

The use of solubility parameters is based on the concept that similar compounds will have an affinity for each other and will be more likely to absorb or dissolve in each other. In the case of elastomers in contact with fluids, mutual solubility is generally to be avoided, i.e., the elastomer is more likely to absorb, swell, and experience significant changes in mechanical properties when in contact with liquids with which it has a high affinity. Here we are estimating the likelihood that the target bioblendstock will be soluble in gasoline. Hansen solubility parameters were obtained from published sources, primarily the HSPiP software [9], but other literature sources were sometimes used. In some cases, solubility parameters were estimated using a chemical group contribution method [10]. These parameters and citations are reported in the online database. Gasoline was modeled as a surrogate blend of seven components, intended to emulate the paraffin, isoparaffin, aromatic, naphthene, and olefin content of typical gasoline as shown in Table 2.

Table 2. Model gasoline composition for solubility parameter analysis.

Alkane	n-octane	10.0%
Alkene	1-octene	7.0%
Isoalkane	iso-pentane	39.0%
Cycloalkane	cyclohexane	8.0%
Cycloalkene	cyclohexene	6.0%
Aromatic	toluene	15.0%
Aromatic	ethylbenzene	15.0%
Total		100.0%
dD= 16.2, dP=0.4, dH=1.0 (MPa ^{1/2})		

Figure 2 shows the three-dimensional solubility parameter space for the pure component oxygenates considered, along with the locations of the model gasoline and water for reference. Because all of these compounds fall within a narrow range of the dispersion parameter, dD (14–18 MPa), it is more informative to view a two-dimensional projection as in Figure 3. Propylene glycol and methanol are the only proposed bioblendstocks with a potential solubility issue. Several poorly soluble compounds that are not proposed bioblendstocks are shown for reference. Solubility parameter theory is not exact, so compounds located near the boundary must be examined experimentally to validate their solubility. However, the poor solubility and water tolerance of methanol in hydrocarbon is well

known, although it can be addressed with co-solvents such as blending of 2.5 vol% isopropyl alcohol with 5 vol% methanol [11].

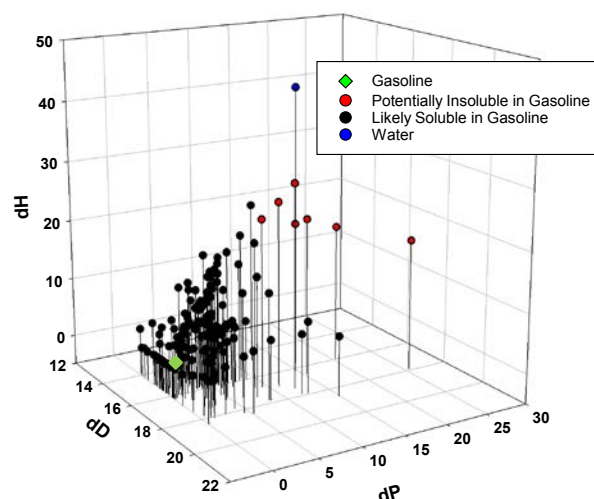


Figure 2. Three-dimensional representation of solubility parameter space for gasoline and oxygenate blendstocks.

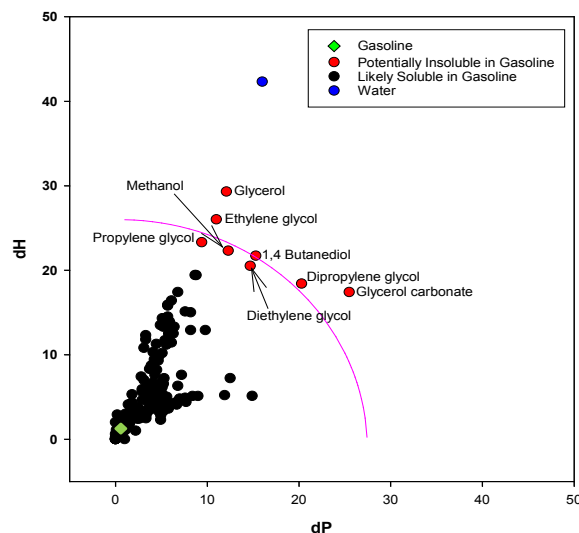


Figure 3. Hydrogen bonding and polarity solubility parameter space.

Health and Physical Hazard Assessment

The Occupational Health and Safety Administration (OSHA) has published a Hazard Communication Standard that defines a set of physical and health hazard categories [12]. Petroleum gasoline presents significant health and physical hazard risks, and our goal in this assessment is to ensure that we do not select bioblendstocks for study that present even greater risks. As an example of the types of risks presented by conventional gasoline, five gasoline samples were selected from our prior and ongoing work [13, 14] and the 20 compounds present at the highest concentrations were determined using ASTM Method D6729 (detailed hydrocarbon analysis). The identity and toxicity of these compounds are shown in Table 3.

Table 3. Toxicity categorization for the 20 highest concentration components of petroleum-derived gasoline.

Compound	CAS#	OSHA Category	Toxicity Information
Isopentane	78-78-4	1	Aspiration and flammability
Methylbenzene (Toluene)	108-88-3	2	Suspected of damaging fertility or unborn child
2-Methylpentane	107-83-5	1	Aspiration
2,2,4-Trimethylpentane	540-84-1	1	Toxic to aquatic life with lasting effects
n-Pentane	109-66-0	1	Aspiration and flammability
n-Hexane	110-54-3	1	Aspiration
m-Xylene	108-38-3	1	Aspiration
o-Xylene	95-47-6	1	Aspiration
p-Xylene	106-42-3	2	Aquatic toxicity
2,3-Dimethylbutane	79-29-8	1	Aspiration
2-Methylhexane	591-76-4	1	Aspiration and toxic to aquatic life with lasting effects
Benzene	71-43-2	1	Carcinogen, may cause genetic defects and cancer
tert-Butylbenzene	98-06-6	2	Aquatic toxicity
Ethylbenzene	100-41-4	1	Aspiration
2,4-Dimethylpentane	108-08-7	1	Aspiration and toxic to aquatic life with lasting effects
Methyl-cyclohexane	108-87-2	1	Aspiration and toxic to aquatic life with lasting effects
n-Butane	106-97-8	1	Flammability
1-Methyl-3-ethylbenzene	620-14-4	2	Aquatic toxicity
3-Methylhexane	589-34-4	1	Aspiration and toxic to aquatic life with lasting effects
2,2-Dimethylpentane	590-35-2	1	Aspiration and toxic to aquatic life with lasting effects

As can be seen, the most common components of gasoline pose several environmental and human health issues, most commonly aspiration, flammability, and toxicity to aquatic life with lasting effects. While benzene is among the 20 most prevalent compounds in gasoline, it is a known human carcinogen (the only one found above trace levels in gasoline) and its concentration in gasoline is limited by the U.S. Environmental Protection Agency (EPA) regulation to a maximum annual average of 0.62 vol% [15]. Methylbenzene, more commonly known as toluene, is suspected of being a reproductive toxin (Category 2) but is not regulated. Nevertheless, a bioblendstock that is a suspected reproductive toxin is highly

undesirable. Conventional transportation fuels present fire and explosion hazards, and the infrastructure for handling these fuels has been designed to accommodate those types of hazards. Therefore, these are not identified as an issue for new bioblendstocks. In this analysis those compounds that are known or suspected carcinogens and reproductive toxins have been eliminated from consideration. In most cases a pure component blendstock safety data sheet will list information regarding these hazard categories. For complex mixtures compositional data were reviewed, but ultimately we are assuming that these can be produced with, for example, benzene levels that meet regulatory requirements.

The OSHA hazard categories describe intrinsic hazards with the material under consideration, but do not cover changes that may occur over time. A possible hazard not covered by these categories is the potential for a compound to form reactive organic peroxides. This is most commonly known to occur for ethers and is generally noted on the safety data sheet.

Corrosion Assessment

The goal of this assessment is to understand if a blendstock or functional group can cause corrosion of storage and distribution apparatus or engine fuel system parts. For pure component blendstocks, the assessment deals with the intrinsic corrosivity of the organic molecule and does not include the potential for impurities such as chloride or sulfur species to cause corrosion. These contaminants are far more likely to cause corrosion issues than the organic molecule itself. Therefore, the corrosion tests used in fuel quality standards for gasoline and diesel fuel (copper and silver corrosion) are not applicable. For the most part, pure component blendstocks are not corrosive to metals. Obvious exceptions are carboxylic acids, and potentially phenol, although alkyl phenols are much less corrosive (note that no phenolic compounds boiling in the gasoline range were proposed as bioblendstocks). A brief literature search was conducted for each pure component functional group examined to determine if there is any evidence for corrosion, and no evidence was found except for carboxylic acids. Thus, carboxylic acids are not considered as potential bioblendstocks. For complex mixtures, we referred to literature data and flagged materials exceeding the total acid number limit on finished biodiesel blendstock intended for blending at up to 20 vol% (0.5 milligram potassium hydroxide per gram maximum) [16]. However, the total acid number can likely be controlled to meet a standard in a developed production process.

Measurement or Prediction of Autoignition Properties

Autoignition chemistry is critical for SI, diesel, and advanced compression ignition combustion. For SI engines, autoignition is undesirable and can occur after the mixture is ignited by the spark when unburned fuel-air mixture autoignites. This is known as engine knock, and if severe can damage an engine. Modern engines have knock sensors and electronic controls to avoid the occurrence of knock, but the primary knock avoidance strategy is spark-timing retard. Retarding spark timing reduces peak temperature and also reduces engine efficiency. Thus, more efficient SI engines can be developed given more highly knock resistant fuels than are available on the market today because spark timing can be maintained at or near the optimal point over a larger portion of the engine's operating range.

For SI engines, the fuel autoignition tendency is measured in two engine tests that produce ratings: RON [17] and Motor octane number (MON) [18]. RON is measured at relatively lower temperature and engine speed than MON and is more representative

of fuel knock resistance in modern and future high-efficiency SI engines [19]. High RON materials, for example, include ethanol with a RON of 109 and toluene with a RON of 120.

Pure component RON values have been measured for many of the bioblendstocks being evaluated. Additionally, because of the small volume requirement (~50 mL), in many cases the derived cetane number (DCN) has been measured instead of RON, and we have applied the inverse correlation between RON and CN shown in Figure 4 to predict RON. This correlation was developed as a part of the research for this report and is based on data for 112 samples, including full boiling range gasolines, primary reference fuels, toluene reference fuels, toluene primary reference fuels, and a broad range of oxygenates. The data are derived from multiple sources [20–25] and include many new CN and RON measurements. The data used to develop this correlation are listed in Table A-1 of the appendix. It has been shown that octane numbers can be derived from CN using linear relationships for fuels with certain range of CN values [23, 26]. However, the CN – RON dependence is significantly non-linear in the regions of both very high and very low DCN values. In Figure 4 the data for high RON (low CN) components is primarily from constant volume testers (DCN). Given the significant error in measuring low DCN values in this type of apparatus, this correlation should only be used for preliminary assessment for high RON (>80) materials.

For many of the proposed bioblendstocks, no experimental information on RON or DCN was available and cost or availability precluded DCN measurement. For hydrocarbon bioblendstocks, we applied a group contribution modeling method to predict RON [27]. Note that a group contribution method is also available for prediction of DCN that is applicable to oxygenates (other than ethers) as well as hydrocarbons [28].

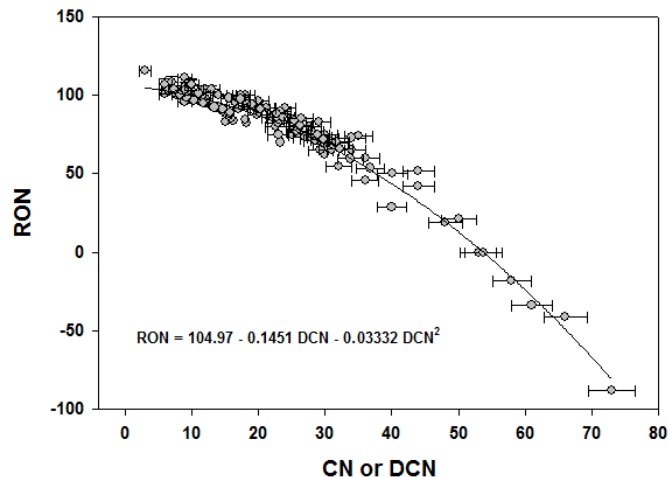


Figure 4. Correlation between RON and cetane number (CN) or DCN developed as a part of this study (predominantly DCN). Error bars are method reproducibility from the ASTM D2699 (RON), D613 (CN), and D6890 (DCN) methods. Note that in ASTM D2699 (RON), reproducibility is only defined for RON values of 90 to 108 and in ASTM D613 for CN values of 40 to 56.

A minimum RON level of 98 was used for screening. This RON level is clearly obtainable using today's hydrocarbon blendstocks and ethanol blending [3], and appears to be adequate for achieving significant improvements and efficiency from the light-duty fleet [2]. Nevertheless, some studies have utilized fuel with 100 or 101 RON to demonstrate the efficiency gains possible with high octane fuel and advanced engines [1,6], and research may ultimately show that a finished fuel RON above 98 is required.

Prediction of Biodegradability

Any compound approved for use in fuel may be manufactured, processed, shipped, and stored in large quantities throughout the country and thus presents a significant risk for release to the environment. Perhaps the two most notorious additions to fuel in the past century, lead alkyls and methyl tert-butyl ether (MTBE), were eventually banned (lead compounds in 1996 nationwide [29] and MTBE in New York and California in 2004, and in 23 other states since then) when widespread soil and groundwater contamination from these compounds was found to present significant risk to human health and the environment [30, 31]. After the deleterious effects of MTBE became apparent, EPA convened a panel of experts who recommended that in order to prevent future similar incidents, the EPA should “conduct a full, multi-media assessment (of effects on air, soil, and water) of any major new additive to gasoline prior to its introduction” [32,33]. The California Air Resources Board requires a “multimedia risk assessment” before adopting new fuel specifications [34].

A complete environmental assessment is beyond the scope of the Tier 1 phase of the Co-Optima program, but screening of the proposed compounds using the EPA EPI Suite™ model is included to assess water solubility and anaerobic biodegradability. EPI Suite is a series of quantitative structure-activity relationship models based on the regression of experimental data to predict the effect of chemical structures on the modeled parameter [35]. This analysis only looks at primary effects—biodegradation of the initial bioblendstock—and not the potential for a biodegradation product to be recalcitrant and toxic.

Biodegradability is a measure of the speed at which compounds can be broken down through the actions of microorganisms such as bacteria. Compounds that biodegrade quickly will be present in the environment for only a short time and thus present little opportunity for impacting human health or the environment, whereas compounds that persist can accumulate and spread. Aerobic biodegradation occurs in the presence of oxygen, most commonly when a compound is exposed to the atmosphere. In contrast, anaerobic biodegradation occurs where contact with the atmosphere is limited and when dissolved oxygen is used up, usually due to the aerobic biodegradation of organic compounds. This is common in groundwater and surface water sites that have been subject to gasoline spills.

Gasoline is generally considered to be biodegradable under aerobic conditions. For example, researchers at Exxon found that gasoline had a half-life of 5 days under conditions favorable for gasoline biodegradation [36]. It has also been shown that gasoline was readily biodegradable under aerobic conditions, with 96% removal in 28 days [37]. EPI Suite finds that many compounds within gasoline are readily biodegradable under aerobic conditions, but not all. The compounds identified as not readily biodegradable in gasoline include benzene, ethylbenzene, and 2,2,4-trimethyl pentane. Thus, while it is possible that some compounds will be so recalcitrant under aerobic conditions that they will present an issue for typical gasoline soil remediation techniques and in aerobic wastewater treatment plants, the EPI Suite readily biodegradable rating is not adequate to screen those that are apparently acceptable (because they are in gasoline and remediation systems are adapted to deal with those compounds) and those that are too difficult to biodegrade and would represent a new remediation problem.

Anaerobic biodegradation of gasoline is slower, on the order of years as opposed to days [38]. Thus in locations where oxygen is limited, such as in groundwater, gasoline is slow to biodegrade. Fortunately,

because most gasoline compounds are relatively insoluble in water, they do not readily enter groundwater and are less mobile in the subsurface than many other chemicals. MTBE was banned because it was found to have severely impacted groundwater [39]. This is because MTBE is both fairly soluble in water (56,000 mg/L) and slow to biodegrade anaerobically [40,41]. Ethyl tert-butyl ether (ETBE) exhibits a similar profile but is slightly more biodegradable and less soluble in water. Compounds that are both difficult to anaerobically degrade and highly soluble present a risk to the environment similar to MTBE. For pure component blendstocks, those likely to cause groundwater contamination were defined as having anaerobic biodegradability the same or worse than ETBE and solubility in water >10,000 mg/L. These were eliminated from further consideration.

Estimating biodegradation potential for thermochemically derived mixtures is much more challenging. We rely on review of very sparse literature, but must accept the fact that little information is available.

Blend Property Testing

Representative bioblendstocks identified as meeting the screening criteria described above were blended into a gasoline blendstock or a gasoline surrogate and tested for vapor pressure (Reid Vapor Pressure [RVP] as DVPE [dry vapor pressure equivalent] by ASTM Method D5191), distillation curve (ASTM Method D86), oxidation stability (ASTM Method D525), as well as measurement of RON (D2699) and MON (D2700). Blending was performed volumetrically. For RVP, distillation, and oxidation stability, the bioblendstocks were blended into a reformulated blendstock for oxygenate blending (RBOB). The properties of the RBOBs are listed in Table A-2 of the appendix. For blend RON and MON, the bioblendstocks were blended into a four-component surrogate gasoline with the composition and properties shown in Table 4. For triptane only a conventional BOB (CBOB) intended for blending E10 in winter months was used for DVPE, distillation, and blending octane measurements. The properties of this blendstock are also listed in Table A-2.

Concentrations of each oxygenate blended into the RBOB and gasoline surrogate were confirmed by gas chromatography. Oxygenates were separated from hydrocarbon matrices with two-dimensional heart-cutting gas chromatography using an Agilent 7890A gas chromatograph equipped with a Deans switch microfluidic switching valve and dual flame ionization detectors. The columns used for compound separation were an Equity-1, 100% polydimethyl siloxane (30 m × 0.25 mm, 0.25 μm df) as the non-polar phase and a Supelco, IL-59 ionic liquid (30 m × 0.25 mm, 0.2 μm df) as the polar phase. A deactivated fused silica restrictor (0.77 m × 0.1 mm) was used to connect from the non-polar column from the Deans switch to the flame ionization detector. The gas chromatograph oven was set to 50°C and held for 15 minutes followed by a temperature ramp of 10°C/min to a final temperature of 250°C. The injection port temperature was set to 250°, and both detectors were set to 275°C. The injection volume was 1 μL with a split ratio of 200:1. Instrument response was calibrated with a gravimetrically prepared mixture of oxygenates at five levels bracketing the expected concentration of the blends. Calibration curves were found to have R² values of 0.998 or greater for all compounds.

Table 4. Composition and properties of gasoline surrogate used for blend RON and MON determination.

Isooctane, vol%	55
n-Heptane, vol%	15

Toluene, vol%	25
1-Hexene, vol%	5
RON	90.3
MON	84.7
Anti-knock index	87.5

Results and Discussion

Screening of Bioblendstocks as Advanced SI Engine Fuels

Out of the 369 pure compounds and 15 mixture bioblendstocks in the database at the time of this analysis, 117 met the requirements for a melting point or cloud point below -10°C and a boiling point between 20°C and 165°C for gasoline-like fuels. The additional criteria described above were applied to eliminate a number of proposed bioblendstocks, including the requirement that RON be 98 or higher. Several known or suspected human carcinogens and reproductive toxins were identified. Only some ethers and one ketone are predicted with some certainty to have anaerobic biodegradation rates and water solubility similar to or worse than MTBE. These include MTBE itself and ETBE. A number of other ethers and ketones, as well as 2,5-dimethylfuran, are suspected of having a poor biodegradation profile but, given the approximate nature of the predictive model, these were not removed from consideration.

The list of bioblendstocks having desirable properties for use in advanced SI engines is shown in Table 5. While predicted properties were used for selection of some of these blendstocks, experimental property data were then acquired and are also presented in Table 5. MON, heat of vaporization (HOV), lower heating value (LHV), density, and water solubility are also reported. The functional group distribution for the most promising bioblendstocks is:

- Alcohols (9) – Alcohols are well known as potential SI fuel blend components, including ethanol, which serves as a benchmark for the performance of bioblendstocks in SI engine fuel.
- Alkanes (1) – Triptane (2,2,3-trimethylbutane) produced from dimethyl ether [42].
- Alkenes (1) – Isooctene or diisobutylene made by dehydration of isobutanol to isobutylene followed by dimerization to a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene [43].

Table 5. List of bioblendstocks with desirable properties as advanced SI engine fuels and measured property data.

Name	Formula	CAS#	RON (D2699)	MON (D2700)	HOV, kJ/kg ^a	LHV, MJ/kg	LHV, MJ/L (at 20°C)	Density, g/L (at 20°C)	Water Solubility, mg/L
<i>Alcohols</i>									
Methanol	CH ₄ O	67-56-1	109	89	1173.5	20.09	15.8	786.4	miscible
Ethanol	C ₂ H ₆ O	64-17-5	109	90	918.2	25.54	20.2	789.3	miscible
n-Propanol ^c	C ₃ H ₈ O	71-23-8	104	89	788.7	30.8	24.7	811.0	miscible
2-propanol ^c	C ₃ H ₈ O	67-63-0	109	97	743.8	30.7	24.1	781.2	miscible
1-Butanol	C ₄ H ₁₀ O	71-36-3	98	85	708.3	33.1	26.8	805.7	68,000
2-butanol	C ₄ H ₁₀ O	78-92-2	107	93	670.5	33.1	26.7	802.6	181,000
2-methylpropan-1-ol (isobutanol)	C ₄ H ₁₀ O	78-83-1	105	90	685.4	33.2	26.6	797.6	85,000
2-methyl-1-butanol	C ₅ H ₁₂ O	137-32-6	101	88.3	613.7	34.69	28.3	814.8	29,700
2-pentanol	C ₅ H ₁₂ O	6032-29-7	99.4	90.8	608.1	34.58	27.8	805.2	44,600
<i>Alkanes</i>									
Triptane (2,2,3-trimethylbutane) ^c	C ₇ H ₁₆	464-06-2	112	101	319.3	44.4	30.8	694.5	29
<i>Alkenes</i>									
Diisobutylene (a mixture of three parts 2,4,4-trimethyl-1-pentene and one part 2,4,4-trimethyl-2-pentene)	C ₈ H ₁₆	25167-70-8	106	86.5	318.2	44.27	31.66	715.1	4
<i>Esters</i>									
Methylacetate	C ₃ H ₆ O ₂	79-20-9	>120	>120	438.7	19.3	17.9	927.1	243,000
Methylbutanoate ^c	C ₅ H ₁₀ O ₂	623-42-7	107.2	105	401.4	26.07	23.25	892.2	15,000
Methylisobutanoate (2-methylpropanoate) ^c	C ₅ H ₁₀ O ₂	547-63-7	103.6	104.7	365.2	28.38	25.04	882.4	9,260
Methylpentanoate ^c	C ₆ H ₁₂ O ₂	624-24-8	103.4	101.1	379.6	28.25	24.99	884.8	2,200
Methyl-2-methylbutanoate ^c	C ₆ H ₁₂ O ₂	868-57-5	110.5	99.1	338.3 ^b	28.08	24.59	875.7	3,200
Ethylacetate	C ₄ H ₈ O ₂	141-78-6	118	>120	399.5	23.79	21.34	894.6	80,000
Ethylbutanoate	C ₆ H ₁₂ O ₂	105-54-4	115.4	106	369.3	28.64	25.17	874.3	4,900
Ethylisobutyrate (2-methylpropanoate) ^c	C ₆ H ₁₂ O ₂	97-62-1	110.3	109.5	342.6	30.44	26.46	869.3	3,200
1-Methylethylacetate (isopropylacetate) ^c	C ₅ H ₁₀ O ₂	108-21-4	>120	--	363.3	25.77	22.47	871.8	29,000
Butylacetate	C ₆ H ₁₂ O ₂	123-86-4	100.8	100	369.3	27.43	24.03	876.0	8,400
Isobutylacetate (2-methylpropylacetate) ^c	C ₆ H ₁₂ O ₂	110-19-0	108.7	112.3	319.4	28.01	24.4	871.2	6,300
Isoamylacetate (3-methylbutylacetate) ^c	C ₇ H ₁₄ O ₂	123-92-2	100.6	97.2	356.4	32.15	27.84	866.1	2,000
<i>Ethers</i>									
Methoxybenzene (anisole)	C ₇ H ₈ O	100-66-3	103	92	428.2	33.5	33.3	989.2	1,040
<i>Furans</i>									
2-Methylfuran/2,5-dimethylfuran mixture (40/60 by weight)	--	--	102	87	--	32.2	29.1	903	2,240
<i>Ketones</i>									
2-Butanone (methyl ethyl ketone)	C ₄ H ₈ O	78-93-3	111	105.5	481.2	31.36	25.08	799.8	223,000
2-Pentanone	C ₅ H ₁₀ O	107-87-9	105.7	103	445.8	33.37	26.75	801.5	43,000
3-Pentanone ^c	C ₅ H ₁₀ O	96-22-0	106.8	--	448.2	33.43	27.08	810.1	45,900
3-Methyl-2-butanone ^c		563-80-4	108.9	102.2	428.4	33.34	26.68	815.0	5,237
Cyclopentanone	C ₅ H ₈ O	120-92-3	101	89.4	504.0	31.99	30.2	944.1	60,000
3-Hexanone ^c	C ₆ H ₁₂ O	589-38-8	101.9	93.5	417.3	34.83	28.61	821.6	14,700
4-Methyl-2-pentanone (methylisobutyl ketone) ^c	C ₆ H ₁₂ O	108-10-1	105.7	105.5	417.3	34.21	27.27	797.1	19,000
2,4-dimethyl-3-pentanone	C ₇ H ₁₄ O	565-80-0	99	92.5	363.4	35.84	28.81	803.9	5,700
Ketone mixture (42.5 wt% 2-pentanone, 11.4 wt% methyl-isobutyl ketone, 30.3 wt% 4-heptanone, 15.8 wt% 2-heptanone)	--	--	99.4	99.6	424 ^b	34.61	27.99	808.7	--
<i>Multifunctional Mixtures</i>									
Vertifuel (60%+ aromatics, Vertimas Process) [49] ^c	--	--	105.7	90.6	--	--	--	810	--
Catalytic conversion of sugar (Virent) [50] ^c	--	--	Up to 110	--	--	--	--	--	--
Mixed aromatics via methanol-to-gasoline [51] ^c	--	--	--	--	--	--	--	--	--
Bioreformate from multistage pyrolysis (Cool Planet) ^c	--	--	108	97	--	39.7	--	887.5	--
Mixed aromatics via catalytic fast pyrolysis ^c	--	--	--	--	--	--	--	--	--
Aromatics and olefins via pyrolysis derived sugars upgrading ^c	--	--	--	--	--	--	--	--	--

^a From Chickos and Acree [52] average value at 25°C unless noted. ^b Measured by differential scanning calorimetry/thermogravimetric analysis method [13]. ^c Not included in blending property study.

- Esters (12) – A significant finding of this work is the large number of low-molecular weight esters with high RON, including esters made by a variety of biochemical, chemical, and hybrid processes.
- Ethers (1) – Anisole is included as a surrogate for methyl aryl ethers that might be produced from a phenolic-rich biomass pyrolysis product.
- Furan mixture – For a typical biomass containing 40 wt% hemicellulose and 60 wt% cellulose a mixture of 2-methylfuran and 2,5-dimethylfuran in the same proportions would be produced [44, 45].
- Ketones (9) – A second significant observation is the promising fuel properties of ketones. Nominally pure components plus one mixture: 42.5 wt% 2-pentanone, 11.4 wt% methyl-isobutyl ketone, 30.3 wt% 4-heptanone, 15.8 wt% 2-heptanone) (produced using chemistry similar to that described in [46]).
- Multifunctional mixtures (6) – typically highly aromatic, although little data are available on product properties. However, given the high predicted aromatic content of these products, the ability to tailor properties such as the boiling point distribution in the process design, and analysis showing competitive economics with biochemical conversion processes [47], these mixtures were included in our list of bioblendstocks with desirable properties.

Bioblendstock Blending Properties

Many of the pure component or simple mixture bioblendstocks listed in Table 5 were used to prepare blends for determination of their effect on RVP, distillation curve, oxidation stability, RON, and MON. To keep the size of the test matrix manageable, a number of bioblendstocks were not tested as blends:

- Seven of the nine alcohols were studied as blends.
- Four esters were selected to explore the structural diversity of this functional group: methyl acetate, ethyl acetate, ethyl butanoate, and butyl acetate.
- Four ketones and a ketone mixture were selected to explore the diversity of this functional group: 2-butanone, 2-pentanone, cyclopentanone, and 2,4-dimethyl-3-pentanone.
- Samples of the multifunctional mixtures were not available for blending.

Blends were prepared in 100% hydrocarbon blendstocks; however, it must be noted that blending into a finished E10 gasoline rather than a blendstock for oxygenate blending (BOB) is also a plausible scenario. This was not investigated in the current study and would yield somewhat different results in some cases because of interactions between the oxygenates. For example, prior studies have shown that blending a butanol isomer with ethanol can reduce or eliminate the increase in RVP observed for ethanol blends [48].

Results for RVP are shown in Figure 5. RVP is a critical gasoline property. A maximum RVP is specified by EPA regulation in the summer months (June 1 to September 15) to reduce evaporative

emissions with a nationwide 9 psi (62.1 kPa) maximum as well as lower levels in reformulated gasoline areas [53]. Maximum RVP is also controlled year round by ASTM standard to prevent hot-weather driveability issues (similar to vapor lock), which can occur year round if a fuel's vapor pressure is too high for ambient conditions. These requirements are likely to also apply to fuels for advanced SI engines. Thus, bioblendstocks that increase vapor pressure are considered undesirable because they increase costs by requiring a lower vapor pressure hydrocarbon blendstock. As shown in Figure 5, the majority of the bioblendstocks tested cause no change or a decrease in RVP when blended into the very low RVP RBOB. The exceptions include ethanol, which is well known to cause gasoline RVP to increase (and at 10 vol% blends in conventional gasoline receives a 1-psi (6.9 kPa) allowance from EPA). Additionally, methyl acetate and methanol cause large increases in RVP.

Figure 6 shows distillation results for the bioblendstocks in the RBOB. The maximum T90 and end point are controlled in ASTM standard specification D4814 to ensure the fuel fully evaporates and to avoid excessive accumulation of fuel in the engine lubricant. Maximum T50 and T10 are also controlled to ensure the fuel is adequately volatile for seasonal ambient conditions, and a T50 minimum is also controlled to ensure the fuel is not excessively volatile for seasonal ambient conditions. Issues with inadequate or excessive volatility lead to poor driveability—poor starting and rough operation in colder weather if the fuel is not adequately volatile, stumbling and misfire in warmer weather if the fuel is excessively volatile [54].

In Figure 6, each chart shows the distillation curve for the base fuel (RBOB) and for the ethanol blend. The RBOB is intended for blending with 10% ethanol to make a Class AA gasoline with a maximum T10 of 70°C, T50 between 77°C and 121°C, and a maximum T90 of 190°C. While driveability effects would ultimately need to be evaluated for any new bioblendstock that was commercialized, these limits can serve as an initial guide. At the 10% blend level, ethanol, methanol, and methyl acetate all depress the front end of the distillation curve significantly; however, they do not depress T50 in this particular gasoline blendstock. The effects of the other bioblendstocks on the distillation curve are very modest.

Larger effects are evident for the 20% blends, with significant T50 depression observed for ethanol and methanol; moderate T50 depression for methyl acetate, ethyl acetate, and 2-butanone (methyl ethyl ketone); and a significant elevation in T50 for anisole. Triptane (at 25 vol%) increases T10 (reduced volatility) and decreases T90 while having no effect on T50. The same effects are observed in 30% blends but are larger in magnitude. Anisole blends at 20% and 30% actually fail the T50 maximum requirement. At 30% there is also significant depression of the boiling point in the T70–T80 region for the butanol and pentanol isomers, diisobutylene, and several of the ketones, although the potential significance of this for vehicle driveability is unknown. Triptane, at the much higher blend level of 50%, increases T10 to over 60°C – potentially causing cold starting and warm up issues if used in the wintertime CBOB.

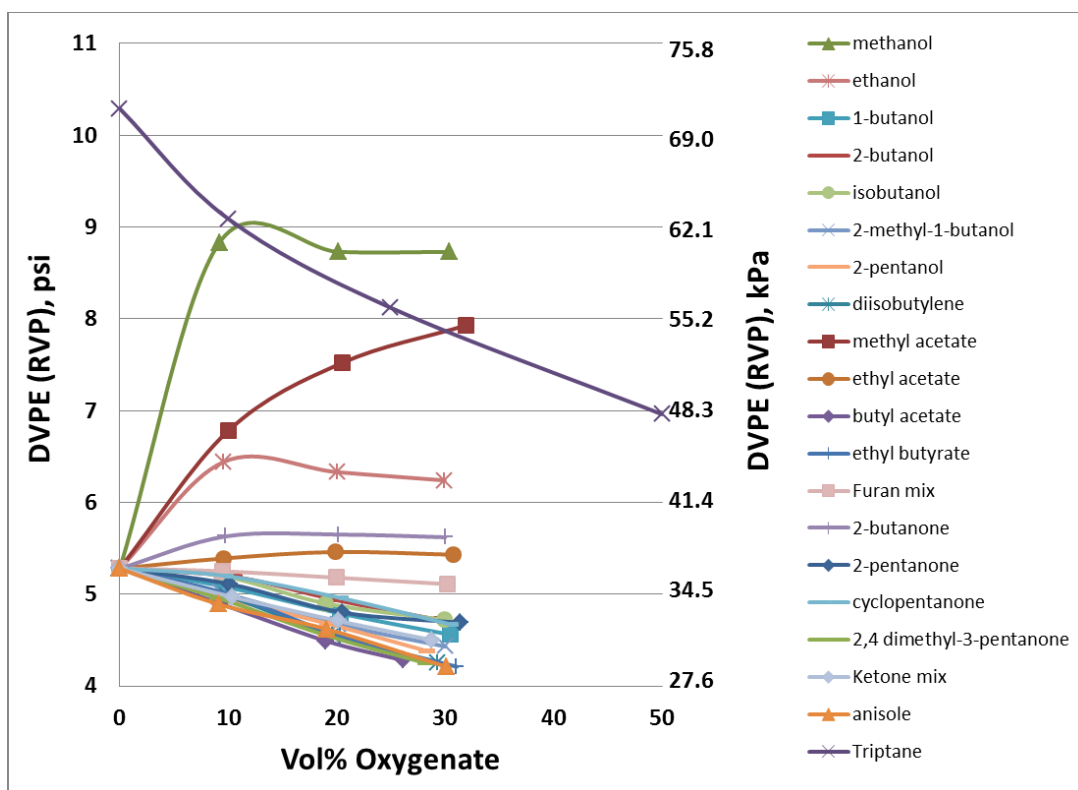


Figure 5. RVP reported as DVPE for blends of the bioblendstocks into the RBOB (triptane blended into CBOB).

The oxidation stability test for gasoline is an indication of the fuel resistance to gum formation in storage. In petroleum gasoline, gum formation is typically caused by oxidation of di-olefinic species – although gum can also originate from other organic functionality or be caused by metal contamination [55]. Stability was measured for the bioblendstocks blended at 20% into the RBOB by the ASTM D525 test. In this pass/fail test, the fuel is placed in a pressure vessel, pressurized to 690 kPa (100 psi) under O_2 , and then heated to 100°C. A breakpoint is defined based on the rate of pressure drop (rate of oxygen consumption). Fuels that do not reach the breakpoint in 240 minutes pass this test. While the test is believed to be an indicator of resistance to gum formation, there is no correlation between time to breakpoint (induction time) and the rate of oxidation or quantity of gum formation.

For the fuels tested here, only the furan mixture and cyclopentanone produced failing results. We have previously reported poor stability for 2,5-dimethylfuran, which undergoes an oxidation reaction to form a gasoline-insoluble liquid [56]. Cyclopentanone and other cyclic ketones are known to undergo self-condensation dehydration reactions under catalytic or high temperature conditions [57], and we speculate that this is occurring here. Note that triptane blends were not tested for stability, although no stability issues are anticipated for isoalkanes.

The bioblendstocks were blended with the four-component surrogate for measurement of their impact on RON and MON. The purpose in using a simple surrogate with well-defined composition is to allow analysis and explanation of the blending octane number results using detailed kinetic simulations, an activity that is ongoing and will be described in a future publication. The blend RON, MON, and octane sensitivity results are shown in Figure 7.

Many of the bioblendstocks are able to elevate the RON of the surrogate to the 98 threshold that we believe applies to fuels for advanced SI engines. This threshold was not achieved by 1-butanol, 2-methyl-1-butanol, 2-pentanol, butyl acetate, 2,4 dimethyl-3-pentanone, or the ketone mixture in the surrogate blendstock. Triptane, with a pure component RON of 112, unexpectedly did not attain the 98 RON level at 25 vol%. Even allowing for the lower RON of the CBOB, all other factors being equal the 25% triptane blend might only have been 93 RON.

Many studies indicate that octane index (OI), as defined in the following equation, is a better metric for knock resistance than RON [1, 58–60]:

$$OI = RON - K S \quad (1)$$

where K is a parameter specific to engine design and operating point [58, 59] and S is octane sensitivity. There is also evidence that K for high efficiency SI engines is equal to -1 or lower under knock-limited conditions. If $K = -1$, then S is essentially added to RON to estimate the octane index, making S a key secondary parameter defining fuel knock resistance. Many studies suggest that a minimum S of 8 or even higher is needed for advanced SI engines. Our surrogate exhibits an S of 5.6, in the typical range for hydrocarbon gasoline blendstocks. As shown in Figures 7e and 7f, alcohols (except 2-pentanol) diisobutylene, the furan mixture, cyclopentanone, and anisole all achieve an S level of 8, while the esters and ketones fail to do so. 2-butanone, ethyl butanoate, and methyl acetate achieved $S > 7$. At 25 vol% triptane had little effect on the CBOB octane sensitivity.

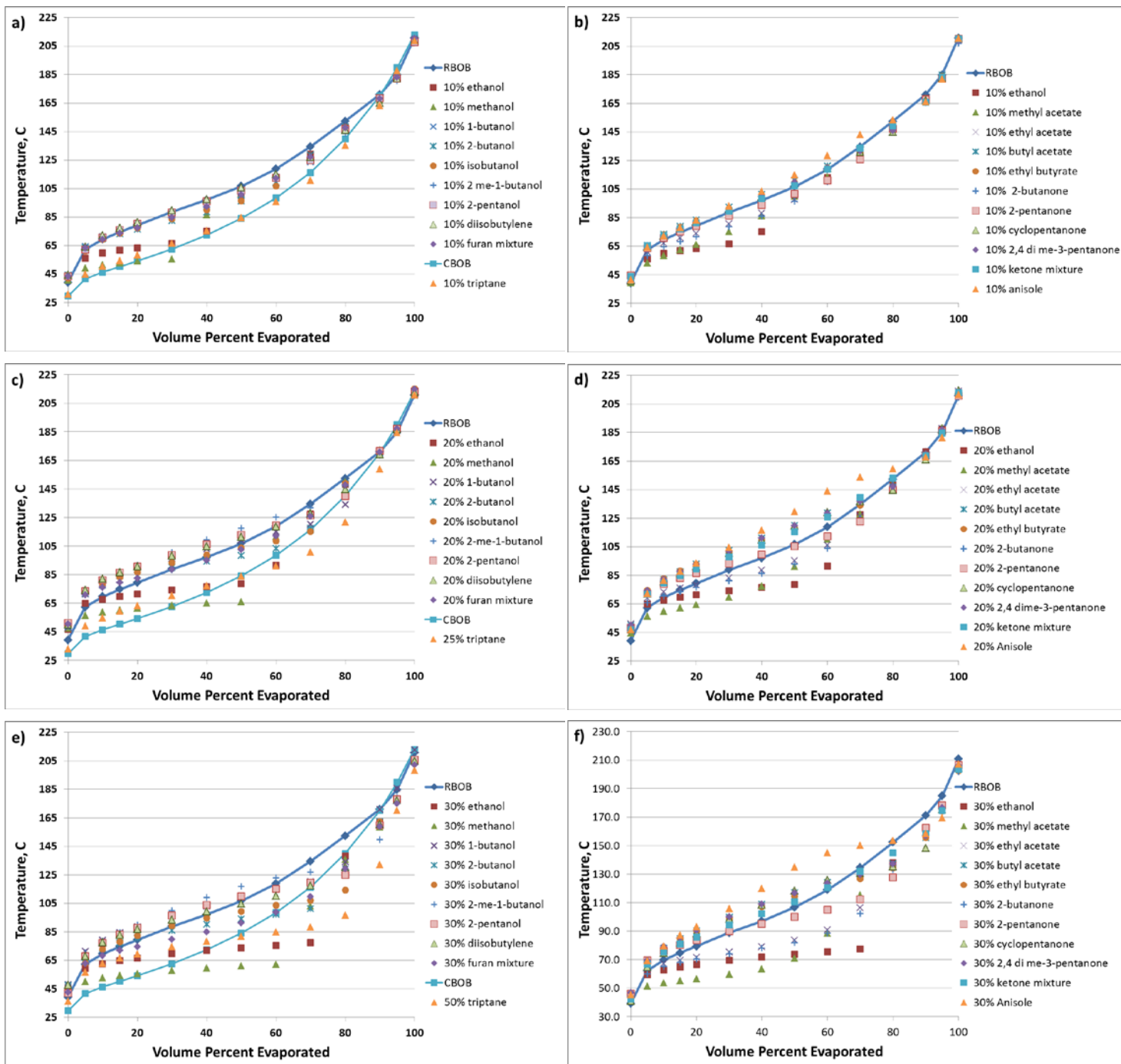


Figure 6. Effect of bioblendstocks on RBOB distillation curve (CBOB for triptane): a) and b) 10% blends, c) and d) 20% blends (25% triptane), e) and f) 30% blends (50% triptane).

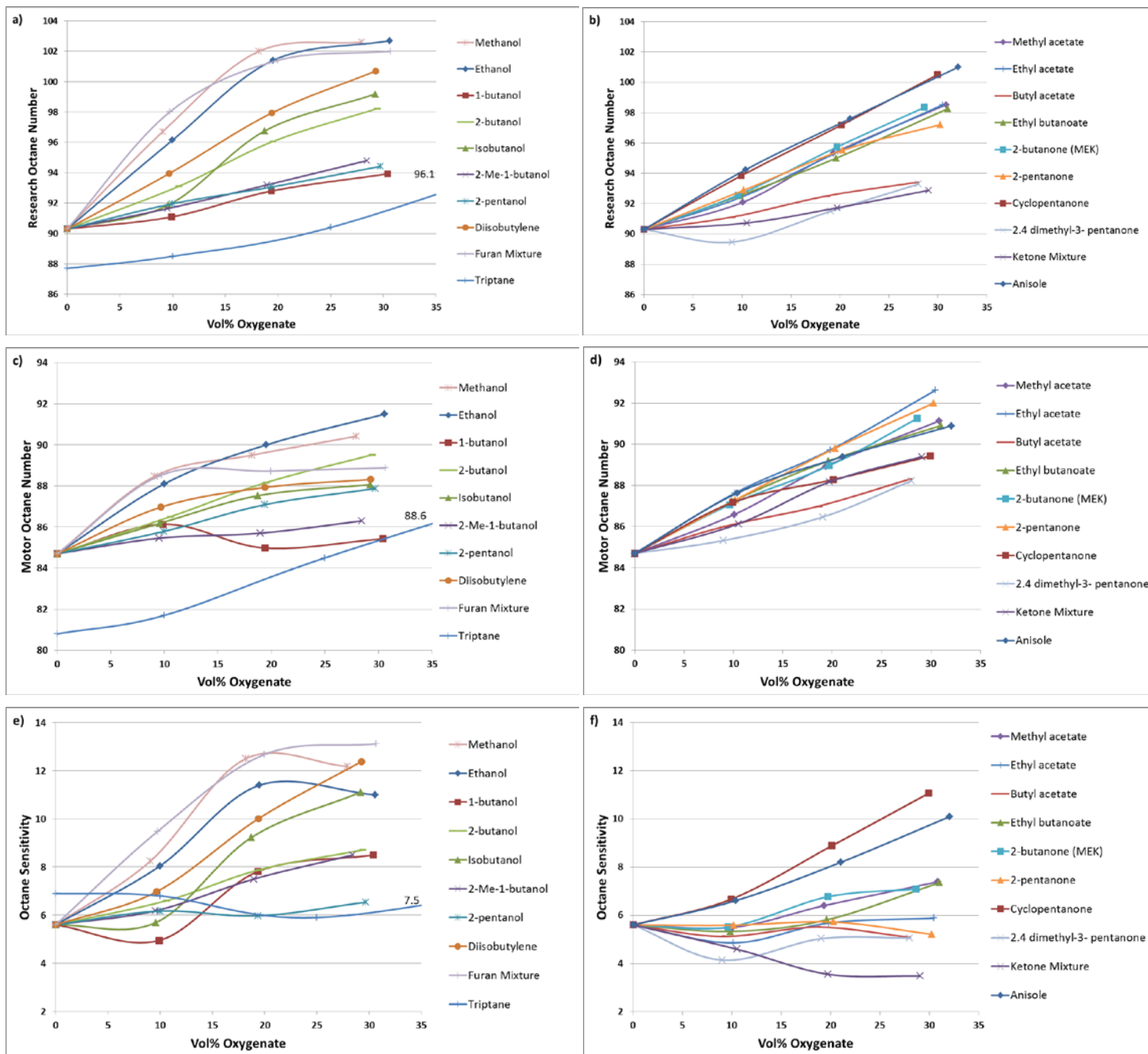


Figure 7. Effect of bioblendstocks on RON, MON, and octane sensitivity when blended into the four-component surrogate. Values given on charts a), c) and e) are for 50 vol% triptane.

Under the assumption that petroleum refiners would use the same blendstock used for blending conventional E10 to blend high octane fuel for advanced SI engines, the blend octane results point to a number of the bioblendstocks having octane blending properties that can meet our minimum requirement of achieving 98 RON and 8 S at the blend levels examined. These qualifying fuels include (from an octane perspective) methanol, ethanol, 2-butanol, isobutanol, diisobutylene, the furan mixture, cyclopentanone, and anisole. While 1-butanol, 2-methyl-1-butanol, butyl acetate, and 2,4-dimethyl-3-pentanone do not appear to have adequate blending RON, the esters and ketones in general do not appear to offer adequate octane sensitivity. It is interesting to note that methyl and ethyl acetate were among the highest RON materials tested, yet their blending RON values are significantly lower than their pure component RON (antagonistic blending). Calculated molar blending RON values for

these two compounds ranged from 100 to 110 in the 10 to 30 vol% range, compared to pure component RON values near 120. This is in contrast to ethanol and diisobutylene whose blending RON values were 112–118 and 120, respectively, higher than their pure component values.

Several of the low RON or low S bioblendstocks were blended into the surrogate along with 10 vol% ethanol as a second bioblend component. A 20 vol% blend of 2-methyl-1-butanol in this E10 exhibited RON > 98 and S > 8. However, blends of 1 butanol into the E10 were unable to meet the minimum RON threshold. Blends of 2-butanone in the E10 exceeded the minimum RON requirement at 10 and 20 vol%, and exceeded the minimum S requirement at 20 vol%. E10 blends of ethyl acetate, 2-pentanone, and the ketone mixture had little effect on octane sensitivity.

Again, under the assumption that these bioblendstocks would be blended with a BOB intended for E10 blending, methanol and methyl acetate increase RVP to a greater degree than does ethanol suggesting that they would be difficult to introduce into the market at these blend levels. Methanol, methyl acetate, and anisole also have a negative effect on the distillation curve, while blends of the furan mixture and cyclopentanone fail the gasoline oxidation stability requirement.

Considering these limitations of the bioblendstocks, those that can be considered as qualifying based on our minimum criteria for use in blending a fuel for advanced SI engines by blending into a BOB intended for blending E10 are:

- Ethanol
- 2-Butanol
- Isobutanol
- 2-Methyl-1-butanol (in E10)
- Diisobutylene
- 2-Butanone (in E10)

It seems likely that if we had tested isopropanol and perhaps n-propanol as blends that they would have also made it on to this list. We did not test branched chain esters, which conceivably could have higher octane sensitivity in blends. It is also possible that the stability of the furan mixture and cyclopentanone could be adequately improved using antioxidant additives making them viable bioblendstocks. The highly aromatic multifunctional mixtures also have potential to meet these requirements. And given the significant increase in octane sensitivity from blending 10% ethanol, it is also possible that those exhibiting low octane sensitivity could be used as a second bioblend component on top of ethanol – as shown above for 2-methyl-1-butanol and 2-butanone. The significant boiling point depression observed for E10 might also allow anisole, which caused a large increase in T50, to be blended. Other approaches could also be envisioned and this analysis is not meant to exclude them from consideration.

Dahmen and Marquardt [61] have described a screening and optimization program based on computer-aided molecular design and computational property prediction as part of the Tailor-Made Fuels from Biomass Program. The SI engine fuels that they proposed based on this approach are furans, ketones, and esters. The furans and ketones that they proposed are also included in Table 5, as are many of the esters. A subsequent study under the same program investigated combustion of 2-methylfuran and 2-butanone as these were considered among the most promising [62]. This model-based design approach is very powerful, and brings in potential production pathways from known bioderived intermediates. Based on our fuel property-based criteria we find that 2-methylfuran may not have adequate storage stability and that 2-butanone may not impart adequate octane sensitivity, and further study is warranted.

While this project under the Co-Optima program has investigated bioblendstocks fuel properties, other projects are examining additional aspects [63]. These include detailed studies of octane sensitivity effects on autoignition [64, 65], fuel property prediction [66], materials compatibility [67], as well as many other aspects.

Summary/Conclusions

A fuel property-based approach to screening of potential bioblendstocks to be used in blending of high-octane fuels for advanced SI engines was developed. To apply this approach, an online fuel property database was developed. Using the database and the screening criteria, a list of promising bioblendstocks based

entirely on bioblendstock properties was developed. Many of these bioblendstocks were blended into hydrocarbon blendstocks to study blending properties. Based on the blend result and assuming a high-octane fuel for advanced SI engines would be produced using hydrocarbon blendstocks available today (BOB intended for E10 blending), ethanol, 2-butanol, isobutanol, and diisobutylene qualify as having minimum acceptable properties for blending of a high-octane advanced SI engine fuel. Additional data and the investigation of additional blending scenarios may show that other bioblendstocks have desirable properties as well.

It is important to note that this screening does not represent a hard downselect for the U.S. Department of Energy's Co-Optimization of Fuels and Engines program. The authors are not endorsing any of the bioblendstocks for commercial scale-up, but rather are using the results from this study together with other studies in the Co-Optima program to prioritize our research and identify candidates that represent the most viable options for near-term market feasibility across a wide range of criteria. Some of the considered bioblendstocks that were not included in the final list may be added as more data become available. Others on the list will likely be removed as additional data on their properties are obtained, along with information on the state of technology for their production and their potential to provide significant life-cycle greenhouse gas emission reductions at reasonable cost. At the same time, additional bioblendstocks not yet considered may be added to this list if they meet the fuel property criteria with promising production processes, scalability, sustainability, and economics.

Contact Information

robert.mccormick@nrel.gov

Acknowledgments

This research was conducted as part of the Co-Optimization of Fuels & Engines (Co-Optima) project sponsored by the U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy, Bioenergy Technologies and Vehicle Technologies Offices. Co-Optima is a collaborative project of several national laboratories initiated to simultaneously accelerate the introduction of affordable, scalable, and sustainable biofuels and high-efficiency, low-emission vehicle engines. Work at the National Renewable Energy Laboratory was performed under Contract No. DE347AC36-99GO10337. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC05-76RL01830. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

The authors wish to thank Michael Charney of the Division of Oil and Public Safety at the Colorado Department of Labor and Employment for performing RON and MON measurements. The authors thank Marathon Petroleum Company LP for supply the RBOB.

References

1. Leone, T.G., Anderson, J.E., Davis, R.S., Iqbal, A., et al., "The Effect of Compression Ratio, Fuel Octane Rating, and Ethanol Content on Spark-Ignition Engine Efficiency," *Environ. Sci. Technol.* 49:10778–10789, 2015.
2. Speth, R.L., Chow, E.W., Malina, R., Barrett, S.R.H., et al.,

- “Economic and Environmental Benefits of Higher-Octane Gasoline,” *Environ. Sci. Technol.* 48:6561–6568, 2014.
3. Anderson, J.E., DiCicco, D.M., Ginder, J.M., Kramer, U., et al., “High Octane Number Ethanol-Gasoline Blends: Quantifying the Potential Benefits in the United States,” *Fuel* 97:585–594, 2012.
 4. Stein, R., Anderson, J., and Wallington, T., “An Overview of the Effects of Ethanol-Gasoline Blends on SI Engine Performance, Fuel Efficiency, and Emissions,” *SAE Int. J. Engines* 6(1):470–487, 2013, doi:10.4271/2013-01-1635.
 5. Chow, E., Heywood, J., and Speth, R., “Benefits of a Higher Octane Standard Gasoline for the U.S. Light-Duty Vehicle Fleet,” SAE Technical Paper 2014-01-1961, 2014, doi:10.4271/2014-01-1961.
 6. Leone, T., Olin, E., Anderson, J., Jung, H., et al., “Effects of Fuel Octane Rating and Ethanol Content on Knock, Fuel Economy, and CO₂ for a Turbocharged DI Engine,” *SAE Int. J. Fuels Lubr.* 7(1):9–28, 2014, doi:10.4271/2014-01-1228. <https://fuelsdb.nrel.gov/fmi/webd#FuelEngineCoOptimization>
 7. Hansen, C.M., “The Three Dimensional Solubility Parameter - Key to Paint Component Affinities I. – Solvents,” *J. Paint Techn.* 39(505):104–117, 1967.
 9. HSPiP Software, computer software, Hansen Solubility Parameters, 2016, <http://hansen-solubility.com/index.html>.
 10. Stefanis, E., and Panayiotou, C., “Prediction of Hansen Solubility Parameters with a New Group-Contribution Method,” *Int. J. Thermophys.* 29(2):568–585, 2008.
 11. Methanol Institute, “Methanol Gasoline Blends,” <http://www.methanol.org/wp-content/uploads/2016/06/Blenders-Product-Bulletin-Final.pdf>, accessed 12/2016.
 12. United States Department of Labor, Occupational Health and Safety Administration, “Guidance for Hazard Determination for Compliance with the OSHA Hazard Communication Standard (29 CFR 1910.1200),” <https://www.osha.gov/dsg/hazcom/ghd053107.html>, accessed 12/2016.
 13. Chupka, G., Christensen, E., Fouts, L., Alleman, T., et al., “Heat of Vaporization Measurements for Ethanol Blends up to 50 Volume Percent in Several Hydrocarbon Blendstocks and Implications for Knock in SI Engines,” *SAE Int. J. Fuels Lubr.* 8(2):251–263, 2015, doi:10.4271/2015-01-0763.
 14. Ratcliff, M., Burton, J., Sindler, P., Christensen, E. et al., “Knock Resistance and Fine Particle Emissions for Several Biomass-Derived Oxygenates in a Direct-Injection Spark-Ignition Engine,” *SAE Int. J. Fuels Lubr.* 9(1):59–70, 2016, doi:10.4271/2016-01-0705.
 15. 40 CFR Parts 80.1220 through 80.1363.
 16. ASTM International, “Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels,” ASTM Standard Specification D6751-15ce1.
 17. ASTM International, “Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuel,” ASTM D2699-15.
 18. ASTM International, “Standard Test Method for Motor Octane Number of Spark-Ignition Engine Fuel,” ASTM D2700-14.
 19. Mittal, V., and Heywood, J., “The Shift in Relevance of Fuel RON and MON to Knock Onset in Modern SI Engines Over the Last 70 Years,” *SAE Int. J. Engines* 2(2):1–10, 2010, doi:10.4271/2009-01-2622.
 20. Yanowitz, J., Ratcliff, M.A., McCormick, R.L., Taylor, J.D., et al., “Compendium of Experimental Cetane Numbers,” (Golden, National Renewable Energy Laboratory, 2014), Report No. NREL/TP-5400-61693, <http://www.nrel.gov/docs/fy14osti/61693.pdf>.
 21. Christensen, E., Yanowitz, J., Ratcliff, M., and McCormick, R.L., “Renewable Oxygenate Blending Effects on Gasoline Properties,” *Energy Fuels* 25(10):4723–4733, 2011.
 22. American Society for Testing Materials, “ASTM Special Publication No. 225: Knocking Characteristics of Pure Hydrocarbons,” May 1958, https://www.astm.org/DIGITAL_LIBRARY/STP/SOURCE_PA/GES/STP225_foreword.pdf.
 23. Bowden, J.N., Johnston, A.A., and Russell, J.A., “Octane-Cetane Relationship, Final Report,” (San Antonio, Southwest Research Institute, 1974), Report No. AFLRL No. 33, 1974.
 24. Sudholt, A., Cai, L., Heyne, J., Haas, F.M., et al., “Ignition Characteristics of a Bio-Derived Class of Saturated and Unsaturated Furans for Engine Applications,” *Proc. Combust. Inst.* 35(3):2957–2965, 2014, <http://dx.doi.org/10.1016/j.proci.2014.06.147>
 25. Naser, N., Yang, S.Y., Kalghatgi, G., and Chung, S.H., “Relating the Octane Numbers of Fuels to Ignition Delay Times Measured in an Ignition Quality Tester (IQT),” *Fuel* 187:117–127, 2017.
 26. Kalghatgi, G., “Auto-Ignition Quality of Practical Fuels and Implications for Fuel Requirements of Future SI and HCCI Engines,” SAE Technical Paper 2005-01-0239, 2005, doi:10.4271/2005-01-0239.
 27. Albahri, T.A., “Structural Group Contribution Method for Predicting the Octane Number of Pure Hydrocarbon Liquids,” *Ind. Eng. Chem. Res.* 42(3):657–662, 2003.
 28. Dahmen, M., and Marquardt, W., “A Novel Group Contribution Method for the Prediction of the Derived Cetane Number of Oxygenated Hydrocarbons,” *Energy Fuels* 29:5781–5801, 2015.
 29. 42 CFR 7545 (n).
 30. NYS Department of Environmental Conservation, “USEPA MTBE Pilot Project Report,” February 2008, http://www.dec.ny.gov/docs/remediation_hudson_pdf/mtbepilot_1.pdf.
 31. Energy Information Administration, “Motor Gasoline Outlook and State MTBE Bans,” <http://www.eia.gov/forecasts/steo/special/pdf/mtbeban.pdf>, accessed 12/2016.
 32. U.S. Environmental Protection Agency, “Achieving Clean Air and Clean Water: The Report of the Blue Ribbon Panel on Oxygenates in Gasoline,” (Washington, DC, 1999), EPA420-R-99-021, <https://www.epa.gov/caaac/achieving-clean-air-and-clean-water-report-blue-ribbon-panel-oxygenates-gasoline>, accessed 12/2016.
 33. 40 CFR Part 79 Subpart F.
 34. California Health and Safety Code, Section 43830.8
 35. McFarland, M.J., Morgan, M.G., et al. *EPA EPI Suite Review Panel, Science Advisory Board (SAB) Review of the Estimation Programs Interface Suite (EPI Suite™)*, September 7, 2007. [http://yosemite.epa.gov/sab/sabproduct.nsf/02ad90b136fc21ef85256eba00436459/CCF982BA9F9CFCFA8525735200739805/\\$File/sab-07-011.pdf](http://yosemite.epa.gov/sab/sabproduct.nsf/02ad90b136fc21ef85256eba00436459/CCF982BA9F9CFCFA8525735200739805/$File/sab-07-011.pdf).
 36. Prince, R., Parkerton, T., and Lee, C., “The Primary Aerobic Biodegradation of Gasoline Hydrocarbons,” *Environ. Sci. Technol.* 41(9):3316–3321, 2007, DOI: 10.1021/es062884d.
 37. Marchal, R., Penet, S., Solano-Serena, F., and Vandecasteele, J.P., “Gasoline and Diesel Oil Biodegradation,” *Oil & Gas Science and Technology—Rev. IFP*, 58(4):441–448, 2003.
 38. Centers for Disease Control, “Gasoline, 5. Potential for Human Exposure,” pp. 117–139. <http://www.atsdr.cdc.gov/toxprofiles/tp72-c5.pdf>, accessed 12/2016.
 39. United States Energy Information Agency, “Eliminating MTBE in Gasoline in 2006,” February 22, 2006. https://www.eia.gov/pub/oil_gas/petroleum/feature_articles/2006/mtbe2006/mtbe2006.pdf Accessed March 15, 2016.

40. Sulfito, J.M., and Mormile, M.R., "Anaerobic Biodegradation of Known and Potential Gasoline Oxygenates in the Terrestrial Subsurface," *Environ. Sci. Technol.* 27:976–978, 1993.
41. Mormile, M.R., Liu, S., and Sulfito, J.M., "Anaerobic Biodegradation of Gasoline Oxygenates: Extrapolation of Information to Multiple Sites and Redox Conditions," *Environ. Sci. Technol.* 28:1727–1732, 1994.
42. Schaidle, J.A., Ruddy, D.A., Habas, S.E., Pan, M., et al., "Conversion of Dimethyl Ether to 2,2,3-Trimethylbutane over a Cu/BEA Catalyst: Role of Cu Sites in Hydrogen Incorporation," *ACS Catal.*, 5:1794–1803, 2015.
43. Kolodziej, R., and Scheib, J., "Bio-isobutanol: The Next Generation Biofuel," *Hydrocarbon Processing*, 79–85, September 2012.
44. Zhang, J., Lin, L., and Liu, S., "Efficient Production of Furan Derivatives from a Sugar Mixture by Catalytic Process," *Energy Fuels*, 26: 4560–4567, 2012.
45. Wang, J., Liu, X., Hu, B., Lu, G., et al., "Efficient Catalytic Conversion of Lignocellulosic Biomass into Renewable Liquid Biofuels via Furan Derivatives," *RSC Adv.*, 4: 31101–31107, 2014.
46. Anbarasan, P., Baer, Z. C., Sreekumar, S., Gross, E., et al., "Integration of Chemical Catalysis with Extractive Fermentation to Produce Fuels," *Nature* 491(7423): 235–239, 2012.
47. Dutta, A., Sahir, A., Tan, E., Humbird, D., et al., "Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels: Thermochemical Research Pathways with In Situ and Ex Situ Upgrading of Fast Pyrolysis Vapors," (Golden, National Renewable Energy Laboratory, 2015), Report No. NREL/TP-5100-62455.
48. Ratcliff, M., Luecke, J., Williams, A., Christensen, E., et al., "Impact of Higher Alcohols Blended in Gasoline on Light-Duty Vehicle Exhaust Emissions," *Environ. Sci. Technol.* 47: 13865–13872, 2013.
49. Narula, C.K., Li, Z., Casbeer, E.M., Geiger, R.A., et al., "Heterobimetallic Zeolite, InV-ZSM-5, Enables Efficient Conversion of Biomass Derived Ethanol to Renewable Hydrocarbons," *Nature Scientific Reports* 5: 16039, 2015, DOI: 10.1038/srep16039.
50. Virent, "Virent BioForm® Gasoline," <http://www.virent.com/wordpress/wp-content/uploads/2015/04/BioForm-Gasoline-Data-Sheet-March-2015.pdf>, accessed 12/2016.
51. Tabak, S., Heinritz-Adrian, M., Brandl, A., McGihon, R., et al., "An Alternative Route for Coal To Liquid Fuel Applying the ExxonMobil Methanol to Gasoline (MTG) Process," Presentation at 2008 Gasification Technologies Conference, Oct 5-8, 2008, <https://www.netl.doe.gov/File%20Library/research/coal/energy%20systems/gasification/gasifiedia/alternate-route-coal-liquid-fuel.pdf>
52. Chickos, J.S., and Acree Jr., W.E., "Enthalpies of Vaporization of Organic and Organometallic Compounds, 1880–2002," *J. Phys. Chem. Ref. Data*, 32: 519, 2003.
53. 40 CFR 80.27.
54. Yanowitz, J., and McCormick, R., "Review: Fuel Volatility Standards and Spark-Ignition Vehicle Driveability," *SAE Int. J. Fuels Lubr.* 9(2):408-429, 2016, doi:10.4271/2016-01-9072.
55. Pradelle, F., Braga, S.L., Martins, A.R.F.A., Turkovics, F., et al., "Gum Formation in Gasoline and Its Blends: A Review," *Energy Fuels* 29: 7753–7770, 2015.
56. McCormick, R.L., Ratcliff, M., Christensen, E., Fouts, L., et al., "Properties of Oxygenates Found in Upgraded Biomass Pyrolysis Oil as Components of Spark and Compression Ignition Engine Fuels," *Energy Fuels* 29: 2453–2461. 2015.
57. Chemical Book, "Cyclopentanone," http://www.chemicalbook.com/chemicalproductproperty_en_cb8709022.htm, accessed 12/2016.
58. Kalghatgi, G., "Fuel Anti-Knock Quality - Part I. Engine Studies," SAE Technical Paper 2001-01-3584, 2001, doi:10.4271/2001-01-3584.
59. Kalghatgi, G., "Fuel Anti-Knock Quality- Part II. Vehicle Studies - How Relevant is Motor Octane Number (MON) in Modern Engines?" SAE Technical Paper 2001-01-3585, 2001, doi:10.4271/2001-01-3585.
60. Orlebar, C., Joedicke, A., and Studzinski, W., "The Effects of Octane, Sensitivity and K on the Performance and Fuel Economy of a Direct Injection Spark Ignition Vehicle," SAE Technical Paper 2014-01-1216, 2014, doi:10.4271/2014-01-1216.
61. Dahmen, M., and Marquardt, W., "Model-Based Design of Tailor-Made Biofuels," *Energy Fuels* 30:1109–1134, 2016.
62. Hoppe, F., Burke, U., Thewes, M., Heufer, A., et al., "Tailor-Made Fuels from Biomass: Potentials of 2-Butanone and 2-Methylfuran in Direct Injection Spark Ignition Engines," *Fuel* 167: 106–117, 2016.
63. Farrell, J., Holladay, J., Wagner, R. "Co-Optimization of Fuels & Engines – FY16 Year in Review" (Golden, National Renewable Energy Laboratory, 2016), <http://www.nrel.gov/docs/fy17osti/67595.pdf>.
64. Sluder, C.S., Szybist, J.P., Ratliff, M., McCormick, R.L., Zigler, B.T. "Exploring the Relationship between Fuel Heat-of-Vaporization and Sensitivity" *SAE Int. J. Fuels Lubr.* 9(1):80-90, 2016, doi:10.4271/2016-01-0836.
65. Westbrook, C.K., Mehl, M., Pitz, W.J., Sjoberg, M. "Chemical Kinetics of Octane Sensitivity in a Spark-Ignition Engine" *Comb. Flame.* 175: 2-15, 2017.
66. Whitmore, L.S., Davis, R.W., McCormick, R.L., George, A., Hudson, C.M. "BioCompoundML: a general biofuel property screening tool for biological molecules using Random Forest Classifiers" *Energy Fuels* 30: 8410–8418, 2016.
67. Kass, M.D., West, B. "Compatibility of Fuel System Elastomers with Bio-blendstock Fuel Candidates Using Hansen Solubility Analysis," SAE Technical Paper No. 2017-01-0802, 2017, doi:10.4271/2017-01-0802.
68. Boot, M., Frijters, P., Luijten, C., Somers, B., et al., "Cyclic Oxygenates: A New Class of Second-Generation Biofuels for Diesel Engines," *Energy Fuels*, 23: 1808–1817, 2009.
69. Christensen, E., Williams, A., Paul, S., Burton, S., et al., "Performance and Properties of Levulinic Esters as Diesel Blend Components," *Energy Fuels* 25(11):5422–5428, 2011.
70. Wallner, T., Ickes, A., and Lawyer, K., "Analytical Assessment of C2–C8 Alcohols as Spark-Ignition Engine Fuels," Proceedings of the FISITA 2012 World Automotive Congress, Lecture Notes in Electrical Engineering 191, DOI: 10.1007/978-3-642-33777-2_2, Springer-Verlag Berlin Heidelberg 2013.
71. Cannella, W., Foster, Gunter, G., and Leppard, W., "FACE Gasolines and Blends with Ethanol: Detailed Characterization of Physical and Chemical Properties," (Alpharetta, Coordinating Research Council, 2014), CRC Report No. AVFL-24, <https://crcao.org/reports/recentstudies2014/AVFL-24/AVFL-24%20FACE%20Gasolines%20Report%20-%20071414.pdf>.

Definitions/Abbreviations

ASTM	ASTM International
BOB	blendstock for oxygenate blending

CBOB	conventional blendstock for oxygenate blending	RBOB	reformulated blendstock for oxygenate blending
CN	cetane number (measured by ASTM Method D613)	RON	research octane number
Co-Optima	Co-Optimization of Fuels and Engines	RVP	Reid vapor pressure, traditional term for vapor pressure measured at 38°C, replaced by DVPE
DCN	derived cetane number (measured by ASTM Method D6890)	S	octane sensitivity (= RON – MON)
dD	solubility parameter for dispersion	SI	spark-ignition
dH	solubility parameter for hydrogen bonding	T10	temperature where 10 wt% of the gasoline has evaporated
dP	solubility parameter for polarity	T50	temperature where 50 wt% of the gasoline has evaporated
DVPE	dry vapor pressure equivalent	T70	temperature where 70 wt% of the gasoline has evaporated
EPA	U.S. Environmental Protection Agency	T80	temperature where 80 wt% of the gasoline has evaporated
ETBE	ethyl tert-butyl ether	T90	temperature where 90 wt% of the gasoline has evaporated
FACE	fatty acid methyl esters	T_b	boiling point
HOV	heat of vaporization	T_m	melting point
K	engine-dependent constant used in calculating octane index	TPRF	toluene primary reference fuel (blend of toluene, isooctane, and heptane)
LHV	lower heating value	TRF	toluene reference fuel (blend of toluene and heptane)
MON	motor octane number	vol%	percent by volume
MTBE	methyl tert-butyl ether		
OSHA	Occupational Safety and Health Administration		
PRF	ethanol/primary reference fuel		

Appendix

Table A-1. Data used for RON–DCN correlation (a = this work). Sample numbers for reference 23 refer to full boiling range gasolines.

Compound	CAS#	CN/DCN	CN Source	RON	RON Source
n-butanol	71-36-3	12	[20]	98	[21]
isobutanol	78-83-1	9	[20]	105	[21]
1-pentanol	71-41-0	18.2	[20]	82	[21]
3 methyl-1-butanol	137-32-6	18.4	[20]	93	[21]
1-hexanol	11-27-3	23.3	[20]	70	[70]
2-heptanol	543-49-7	25	[20]	75	a
3,7-dimethyl-1-octanol	106-21-8	29.3	[20]	64.9	a
linalool (3,7-dimethyl- 1,6-octadien-3-ol)	78-70-6	20	a	96.7	a
n-pentane	109-66-0	30	[20]	62	[22]
hexane	110-54-3	48	[20]	19	[22]
heptane	142-82-5	53	[20]	0	[22]
octane	111-65-9	58	[20]	-18	[22]
nonane	111-84-2	61	[20]	-34	[22]
decane	124-18-5	66	[20]	-41	[22]
dodecane	112-40-3	73	[20]	-88	[22]
2-methylpentane	107-83-5	35	[20]	74	[22]
2,2-dimethylbutane	75-83-2	24	[20]	92	[22]
2-methylhexane	591-76-4	44	[20]	42	[22]
3-methylpentane	96-14-0	30	[20]	75	[22]
2,4-dimethylpentane	108-08-7	29	[20]	83	[22]
2-methylheptane	592-27-8	50	[20]	21	[22]
3-methylhexane	591-76-4	44	[20]	52	[22]
3-ethylpentane	617-78-7	34	[20]	65	[22]
isooctane	540-84-1	11	[20]	100	[22]
cyclopentane	287-92-3	6	[20]	101	[22]
methylcyclopentane	96-37-7	17	[20]	91	[22]
cyclohexane	110-82-7	15	[20]	83	[22]
ethylcyclohexane	1978-91-7	36	[20]	46	[22]
methyl cyclohexane	108-87-2	23	[20]	75	[22]
1-hexene	592-41-6	26	[20]	76	[22]
1-heptene	592-76-7	32	[20]	55	[22]
1-octene	111-66-0	40	[20]	29	[22]
trans-3-octene	14919-01-8	34	[20]	73	[22]

Compound	CAS#	CN/DCN	CN Source	RON	RON Source
2,2,4-trimethyl-1-pentene	107-39-1	10	[20]	106	[22]
ocimene (3,7-dimethyl- (3E)-1,3,6-octatriene)	3779-61-1	28	a	72.9	a
pinene	80-56-8	22.6	a	80	a
3-carene	13466-78-9	26.9	a	73.5	a
toluene	108-88-3	3	[20]	116	[22]
1,2,4-trimethylbenzene	95-63-6	9	[20]	111	[22]
tetralin	119-64-2	9	[20]	96	[22]
n-butylbenzene	104-51-8	12	[20]	104	[22]
cyclopentanone	120-92-3	9	a	101	[22]
cyclohexanone	108-94-1	10	[68]	101	[22]
3-pentanone	96-22-0	10	a	106.8	a
2-heptanone	110-43-0	30	[20]	69	a
anisole	100-66-3	6.4	[56]	103	a
4-methyl anisole	104-93-8	7.4	[56]	104	a
furan	110-00-9	7	[24]	108.6	[22]
2-methyl furan	534-22-5	8.9	[24]	103	[22]
2,5 dimethyl furan	625-86-5	11	[24]	101.3	[22]
methyl pentanoate	624-24-8	13	[20]	104	a
methyl butyrate	623-42-7	6	[20]	107.2	a
ethyl hexanoate	123-66-0	28	a	77	a
methyl hexanoate	106-70-7	24	[20]	87.3	a
butyl levulinate	2052-15-5	14	[69]	100	[21]
methyl tetrahydrofuran	96-47-9	22	[24]	86	[21]
5066		16.2	[23]	84.1	[23]
5066-2		16	[23]	85.3	[23]
5066-3		15.6	[23]	86.7	[23]
50664		15.1	[23]	88.3	[23]
5066-5		14.7	[23]	89.9	[23]
5067-6		14.2	[23]	91.6	[23]
5067-7		13	[23]	93.2	[23]
5067-8		12	[23]	95.1	[23]
5067-9		10.3	[23]	96.8	[23]
5067-10		9.2	[23]	98.5	[23]
5068		7.8	[23]	100	[23]
5224		18.1	[23]	84.5	[23]

Compound	CAS#	CN/DCN	CN Source	RON	RON Source
4656		14	[23]	93	[23]
5242		8.2	[23]	100.1	[23]
5026		15.8	[23]	88.7	[23]
5208		12.1	[23]	95.5	[23]
5233		11.8	[23]	94.9	[23]
5244		14.6	[23]	91.4	[23]
5042		15.6	[23]	88.3	[23]
5050		15.7	[23]	88.9	[23]
5252		13.4	[23]	92.3	[23]
PRF 0		53.8	[25]	0	[25]
PRF 50		40.1	[25]	50	[25]
PRF 60		36.1	[25]	60	[25]
PRF 70		31.6	[25]	70	[25]
PRF 80		27.7	[25]	80	[25]
PRF 90		23.3	[25]	90	[25]
PRF 100		17.4	[25]	100	[25]
TRF 40		36.7	[25]	53.7	[25]
TRF 45		33.8	[25]	59.7	[25]
TRF 50		31	[25]	65.6	[25]
TRF 55		28.6	[25]	71.3	[25]
TRF 60		25.8	[25]	76.9	[25]
TRF 65		22.9	[25]	82.3	[25]
TRF 70		19.8	[25]	87.5	[25]
TPRF 60-10		32.2	[25]	66.2	[25]
TPRF 60-20		29.1	[25]	73.3	[25]
TPRF 60-30		26.2	[25]	79.9	[25]
TPRF 60-40		22.7	[25]	85.9	[25]
TPRF 70-10		28.9	[25]	74.8	[25]
TPRF 70-20		26.3	[25]	80.7	[25]
TPRF 70-30		23.7	[25]	86.1	[25]
TPRF 70-40		19.9	[25]	91	[25]
TPRF 80-10		25.4	[25]	83.5	[25]
TPRF 80-20		22.8	[25]	88	[25]
TPRF 80-30		19.8	[25]	92.2	[25]
TPRF 80-40		16.5	[25]	96.1	[25]

Compound	CAS#	CN/DCN	CN Source	RON	RON Source
TPRF 90-10		21.1	[25]	92	[25]
TPRF 90-20		18.3	[25]	95.3	[25]
TPRF 90-30		15.6	[25]	98.3	[25]
FACE A [71]		26.4	[25]	85.3	[25]
FACE F [71]		19.1	[25]	94.4	[25]
FACE I [71]		31.7	[25]	70.3	[25]
FACE J [71]		29.7	[25]	71.8	[25]
Coryton (full boiling range)		17.3	[25]	97.5	[25]
Haltermann (full boiling range)		20.3	[25]	91	[25]

Table A-2. Reformulated blendstock for oxygenate blending properties.

Property	RBOB	CBOB ^a
DVPE (RVP), psi	5.28	10.29
RON	87.5	87.8
MON	80.6	80.8
Anti-knock index	84.1	84.3
Oxidation stability (D525), P/F	Pass	--
Heat of Vaporization, kJ/kg	358.8	--
Density at 25°C, g/mL	0.7438	0.7142
Detailed Hydrocarbon Analysis		
Average Molecular Weight, g/mol	100.3	--
Paraffin, vol%	11.6	--
i-Paraffins, vol%	40.9	--
Aromatics, vol%	33.7	--
Naphthenes, vol%	5.97	--
Olefins, vol%	7.06	--
Distillation (D86)		
T10, °C	70	46
T50, °C	107	84
T90, °C	171	170

^aUsed for triptane blends only.