

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

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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.

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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, 2, 3, 4, 5, 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

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

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.

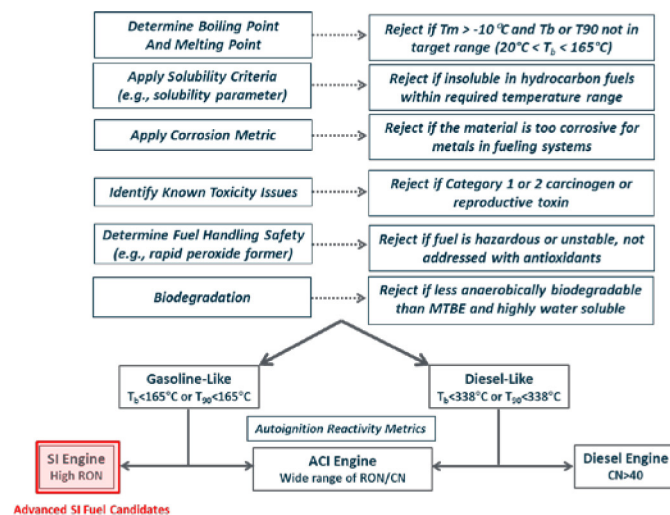


Figure 1. Decision framework for application of Tier 1 metrics for bioblendstock screening and categorization.

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.

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 bioblendstock 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.

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].

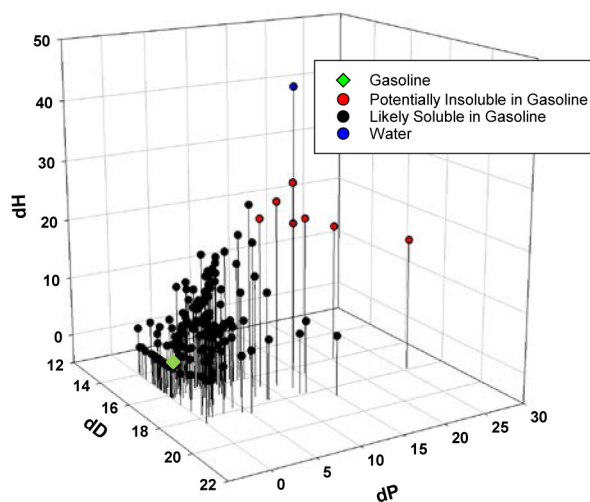


Figure 2. Three-dimensional representation of solubility parameter space for gasoline and oxygenate blendstocks.

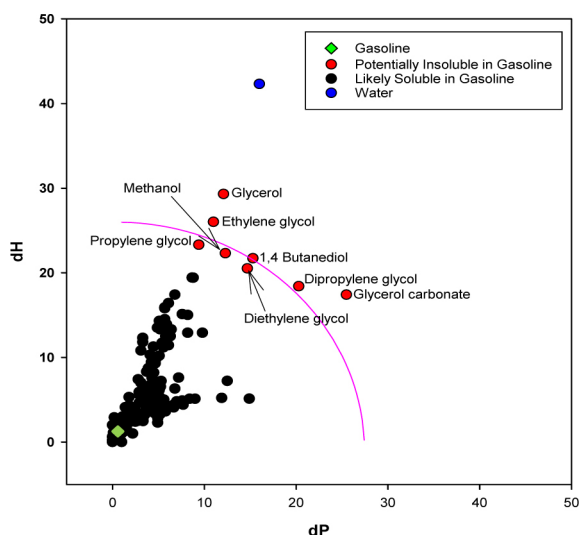


Figure 3. Hydrogen bonding and polarity solubility parameter space.

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.

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.

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

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,

21, 22, 23, 24, 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].

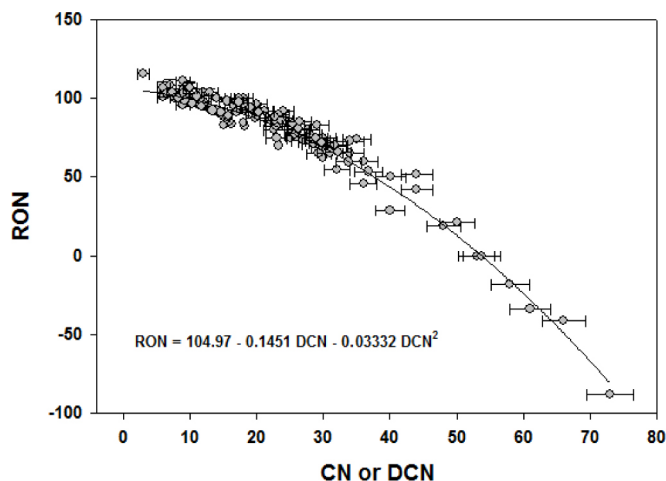


Figure 4. Correlation between RON and cetane number (CN) or DCN developed as a part of this study (predominantly DCN). Error bars are method reproducibility from the ASTM D2699 (RON), D613 (CN), and D6890 (DCN) methods. Note that in ASTM D2699 (RON), reproducibility is only defined for RON values of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