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Screening of Potential Biomass-Derived Streams as Fuel Blendstocks for Mixing Controlled Compression Ignition Combustion

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Abstract

Mixing controlled compression ignition, i.e., diesel engines are efficient and are likely to continue to be the primary means for movement of goods for many years. Low-net-carbon biofuels have the potential to significantly reduce the carbon footprint of diesel combustion and could have advantageous properties for combustion, such as high cetane number and reduced engine-out particle and NO_x emissions. We developed a list of over 400 potential biomass-derived diesel blendstocks and populated a database with the properties and characteristics of these materials. Fuel properties were determined by measurement, model prediction, or literature review. Screening criteria were developed to determine if a blendstock met the basic requirements for handling in the diesel distribution system and use as a blend with conventional diesel. Criteria included cetane number ≥40, flashpoint ≥52°C, and boiling point or T90 ≤338°C. Blendstocks needed to be soluble in diesel fuel, have a toxicity no worse than conventional diesel, not be corrosive, and be compatible with fuel system elastomers. Additionally, cloud point or freezing point below 0°C was required. Screening based on blendstock properties produced a list of 12 that were available as fuels or reagent chemicals or could be synthesized by biofuels production researchers. This group included alkanes, alcohols, esters, and ethers. These candidates were further examined for their impact fuel properties upon blending with a conventional diesel fuel. Blend properties included cetane number, lubricity, conductivity, oxidation stability, and viscosity. Results indicate that all 12 candidates can meet the basic requirements for diesel fuel blending, although in some cases would require additive treatment to meet requirements for lubricity, conductivity, and oxidation stability.

Introduction

Diesel fuel used in mixing-controlled compression-ignition (MCCI) engines is the primary energy source for freight transport globally and is second only to gasoline in terms of liquid fuel demand [1]. In the United States, diesel demand is projected to be the same in 2050 as in 2017 despite a 50% increase in heavy-duty truck miles because of substantial improvements in vehicle fuel economy [1]. Global diesel demand is forecast to experience continuous growth through 2040, becoming the single largest liquid fuel segment [2]. Global road freight activity is projected to increase by a factor of 2.4 by 2050, with 90% of heavy trucks powered by diesel engines [3]. Heavy-duty truck fuel economy improvements along with the use of lower-net-carbon fuels are critical to meeting sustainability goals for this sector [3]. A significant component of truck fuel economy improvement will be improved engine efficiency, and fuel properties may play a significant role. A higher degree of premixing can produce faster heat release, leading to improved efficiency, and this can be enabled by a more volatile, less ignitable fuel [4]. Fuels can also shift the oxides of nitrogen-particulate matter trade-off to lower emission levels [5] [6], which can be leveraged in optimized engine calibrations to improve efficiency [5] [7].

The U.S. Department of Energy's Co-Optimization of Fuels and Engines (Co-Optima) project is developing the scientific and technical foundation to maximize performance and carbon efficiency. Because MCCI (or diesel) engines will play an important role in the economy for decades into the future, work has been initiated to identify potential fuel blendstocks that could be produced from renewable resources and that have a range of chemical structures. Ongoing work will examine the impact of chemical structure on fuel properties and engine performance. In this paper we describe the development of fuel screening criteria for selection of MCCI blendstocks and the results of fuel property measurements for blendstocks in neat form and as blends with a commercial diesel fuel or a diesel surrogate.

Blendstock Screening Approach

Like the approach used previously for spark-ignition engine fuels, [8] a three-tiered fuel screening approach was developed for MCCI combustion fuels. The objective of Tier 1 screening is to identify materials that can first, be used as a fuel, and second, have the required and desirable properties for MCCI combustion. Tier 1 criteria include the physical properties of boiling point, melting point, and solubility in water, as well as basic safety criteria such as flash point, toxicity, peroxide formation potential, and corrosivity. Cetane number (CN) was used as the autoignition metric. Lower heating value and soot formation tendency quantified by yield sooting index (YSI) [9] are reported. The Tier 1 criteria and their limits are shown in Table 1. Blendstocks falling outside the defined ranges for these properties were excluded from consideration in the current exercise.

Tier 2 level screening is focused on properties of the blendstocks blended into petroleum diesel or a simple diesel surrogate. These properties include the impact of the blendstock on distillation curve, viscosity, lubricity, conductivity, oxidation stability, cloud point, solubility in conventional diesel, and blending CN. Table 2 lists Tier 2 criteria and their limits. Tier 3 research will include detailed engine combustion studies, as well as analysis of economics, life-cycle sustainability, and commercialization issues. These attributes are being assessed in subsequent tasks in the program. A discussion of each Tier 1 and Tier 2 property, how they are measured or estimated, and how the limit was determined is provided in the Methods section.

Methods

Lists of potential biofuel blendstocks were developed based on published reports and ongoing research. This list could not be all inclusive but represents major chemical families and a range of established and emerging conversion pathways. Tier 1 property values were obtained from the literature, measurement, or estimation as described below. Details on blendstock identity, composition, and properties have been made accessible in an open-source online database [10]. The database includes results for hundreds of pure compounds, tens of mixture blendstocks, and several hundred finished fuel blends.

Melting Point, Boiling Point, and Flashpoint Values

Melting point (T_m) was used to screen for compounds with $T_m < 0°C$, a metric chosen to ensure the blendstock could be handled and blended in a terminal environment and would not have a large effect on finished fuel cloud point. For wintertime use in some areas, the blend level of a 0°C T_m blendstock could be limited. Cloud point is the temperature where, upon cooling, visible crystals first appear in a multicomponent fuel. Cloud point is widely used as a measure of the low-temperature operability limit of a diesel fuel (although with the use of flow improver additives operability at significantly lower temperatures can be achieved) [11] [12] [13]. Boiling point (T_b) is limited to prevent the presence of components that do not fully evaporate and burn in low-speed, low-load duty cycles, leading to high levels of lube oil dilution and in-cylinder carbon deposits. Boiling point values were used to select compounds boiling below (or mixtures having T90 below) 338°C, the diesel T90 limit in ASTM D975, which is the Standard Specification for Diesel Fuel Oils. Note that blendstocks boiling near this limit cannot be blended into a conventional petroleum diesel fuel in significant volume and still meet the T90 limit for the finished blend, so in practice, a

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

Property	Description/Significance	Limit
IUPAC name & synonyms; CAS#	Unambiguous identification of blendstock	
C, H, N, O, and S content	Chemical composition	
Boiling point or distillation curve (mixtures)	Must boil below the T90 limit for diesel in ASTM D975	<338°C
	Meets T90 requirement in ASTM D975	T90<338°C
Flashpoint	Safety when handling in terminal and for finished fuel as defined in ASTM D975	>52°C
Melting point (pure component) or cloud point (mixtures)	Blendstock handling in terminal and for finished fuel	<0°C
Solubility in water	Prevent phase separation in wet distribution system	<20 g/L
Toxicity	Occupational Safety and Health Administration (OSHA) category 1 or 2 for acute toxicity, carcinogenicity, and reproductive toxicity excluded	
Peroxide former	Safety in handling	Report
Corrosion	Pure component: Blendstocks that are corrosive to metals not considered	Carboxylic acids and acidic phenolics excluded
	Mixture: Highly acidic blendstocks are excluded. Total acid number (TAN) limit from ASTM D6751	TAN<0.3 mg KOH/g
Autoignition metric (CN)	Critical metric for determining if acceptable for combustion in diesel engines	$\geq$40
Biodegradation	Screening of anaerobic biodegradation and water solubility. Lower biodegradability/ water solubility than methyl tert-butyl ether (MTBE)	

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TABLE 2 Tier 2 evaluation criteria for blendstocks blended into diesel fuel or 7-component surrogate.

Property	Description/Significance	Limit
Distillation T90	Meets T90 in ASTM D975 (ASTM D86 or D2887)	T90<338°C
Flashpoint	Safety when handling in terminal and for finished fuel as defined in ASTM D975 (ASTM D93)	≥52°C
Cloud point	Low-temperature operability of finished fuels also identifies blendstocks poorly soluble in hydrocarbon at low temperature (ASTM D5773)	<0°C
Viscosity	Viscosity limits are those in ASTM D975 (ASTM D445)	Between 1.9 and 4.1 cSt at 40°C
Lubricity	Minimum requirement on High Frequency Reciprocating Rig test is from ASTM D975 (ASTM D6079)	≤520 µm
Conductivity	Limit from ASTM D975 (ASTM D2624)	≥25 pS/m
Oxidation stability	Requirement from Top-Tier Diesel program (ASTM D7545)	>60 min
Blend cetane number	Minimum requirement in ASTM D975 (ASTM D8183)	≥40

blendstock to be blended at 20 or 30 volume percent (vol.-%) would likely need to have a much lower T_b. Flashpoint is a critical safety parameter for diesel fuel during handling, storage, and transportation and as a vehicle fuel. The flashpoint is the temperature at which a flammable fuel-air mixture forms above the liquid fuel. The formation of a flammable mixture above the liquid fuel creates the risk of accidental combustion in fuel storage tanks at terminals and retail stations and on board a vehicle. The limit of 52°C minimum in ASTM D975 ensures safe fuel handling under almost all ambient conditions and is also required by fire safety regulations [14].

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 (biomass hydrothermal liquefaction products, 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 D2887). Cloud point was measured for mixtures using ASTM Method D5773. Flashpoint was measured using ASTM Method D93, Method D7094, or estimated using the method of Prugh [15] or that of Butler and co-workers [16].

Solubility in Water

Because diesel is handled in a wet system, blendstocks that can be extracted into the water phase are undesirable due to water contamination risks and because the remaining fuel might not meet performance requirements. The diesel fuel distribution system, which includes all aspects of storage and delivery until the fuel is ultimately burned in an engine, has the potential to expose fuels to water. Free water exists at the bottom of storage tanks at refineries, terminals, and retail sites and at low points along pipeline routes or along the bottom of pipelines themselves [17]. This contrasts with the gasoline distribution system where finished product tanks at terminals and retail are dry because of the potential for phase separation of gasoline ethanol blends. Christensen and coworkers evaluated the extent to which oxygenates could be extracted from gasoline by a water layer [18]. They observed that a significant fraction of C2 to C4 alcohols were extracted while very little of the C5 alcohols was extracted. The pentanols exhibited a water solubility of 2.5% or lower, and based on this, we have selected a water solubility limit of 2%, or 20 g/L. No similar study appears to have been performed for diesel fuels. Water solubility was acquired using SciFinder, or if unavailable was predicted using EPI Suite™. In a few cases, water solubility was measured. Water was saturated with each of the blendstocks by adding deionized water to the samples at a ratio of 1:5 by volume and shaking thoroughly for >1 minute. The mixed samples were left overnight to separate and the amount of blendstock in the aqueous layer was determined by gas chromatography/ mass spectrometry.

Health and Physical Hazard Assessment

The Occupational Safety and Health Administration (OSHA) has published *Hazard Communication Guidance for Manufacturers, Importers, and Employers*, which defines a set of physical and health hazard categories and provides explanations of each hazard category [19]. Petroleum diesel presents significant health and physical hazard risks, and our goal in this assessment is to ensure that we do not select blendstocks for study that present even greater risks than petroleum diesel fuel. The limitation on flashpoint described above is intended to produce fuels with similar fire safety hazard to petroleum diesel. Compounds or mixtures that are known health hazards and are OSHA category 1 or 2 for Acute Toxicity, Carcinogenicity, and/or Reproductive Toxicity were excluded.

Certain compounds, especially ethers, can form peroxides that can precipitate from solution during solvent evaporation to form shock-sensitive crystals that represent an explosion hazard [20]. For pure compounds, the peroxide formation potential may be included in the Safety Data Sheet and can be prevented using inhibitor (antioxidant) additives. For our purposes it is critical that peroxide formers be identified so that research can be conducted safely and, if such a blendstock is ever commercialized, it always contains suitable antioxidant additives.

Corrosion Assessment

Fuels should not cause corrosion of distribution infrastructure or vehicle fuel systems. For nominally pure compounds, corrosion is the intrinsic corrosivity of the organic molecule. This does not include impurities such as chloride or sulfur species known to cause corrosion and that might be present as residues or byproducts of a manufacturing process. These contaminants are far more likely to cause corrosion issues than the organic molecule itself and are the species controlled by the standard copper corrosion test (ASTM D130) that is included in the ASTM D975 standard for ensuring fuel quality of diesel fuel. Organic compounds generally are not corrosive to metals except for carboxylic acids, and potentially acidic phenolics, although alkyl phenols are much less corrosive than phenol itself. Thus, carboxylic acids and acidic phenolics are not considered as potential blendstocks (no carboxylic acids or phenolic compounds were proposed as diesel blendstocks; however, they might be present in mixtures). For complex mixtures we are limiting total acid number (TAN) measured by ASTM D664 to no more than 0.3 mg KOH/g). This is based on the TAN limit of 0.5 mg KOH/g established for B100 biodiesel to be used in preparing 20 vol.-% blends [21] but lowered to accommodate blendstock blending up to 30 vol.-%. Note that the TAN can likely be controlled to meet a standard in a developed production process.

Measurement or Prediction of Cetane Number

A high reactivity for autoignition is a critical diesel fuel property. The fuel must ignite with minimal ignition delay upon being injected into hot, compressed air and residual gases near top dead center. For fuels in the United States that meet the ASTM D975 standard, this is ensured by requiring that CN has a minimum value of 40, while in the European Union the EN590 standard requires a minimum of 51. CN is a measure of ignition delay-the time between start of injection and fuel autoignition. Higher CN values indicate shorter ignition delay. It affects ignition timing, heat release rates, emissions, and engine cold starting such that engines do not operate as designed if CN is too low [22] [23] [24] [25]. Cetane number is historically measured in an engine test by ASTM Method D613. In recent years several different constant-volume ignition delay measurement devices have also been allowed by D975 for measurement of cetane number. These are referred to as derived (DCN) or indicated (ICN) cetane numbers. Cetane numbers used for blendstock screening were measured by D613, D6890 (DCN), or D8183 (ICN) and are indicated as such in our public database; however, they will not be distinguished in this work and are all referred to as CN.

Initial screening was accomplished applying the criteria detailed in Table 1 (CN ≥ 40), with CN in many cases estimated using a group contribution method [26]. Because we were unsure of the absolute accuracy of this prediction, we applied a criterion of greater than 30 specifically for predicted CN to ensure that we captured any compounds for which the prediction was poor and could potentially have CN ≥40. We then acquired and measured the CN of the compounds with predicted CNs above 30. Note that in many cases the compounds of interest were not available from commercial chemical suppliers or were not offered at a price considered reasonable for this program.

It should be noted that CN improver additives are available and widely used in some markets. An example of a CN improver additive is 2-ethyl hexyl nitrate. While additive response depends significantly on fuel characteristics, adding 500 ppm (mass) of 2-ethyl hexyl nitrate can increase CN by approximately two. Economically, CN improver additives are used to increase CN by two or three numbers [27]. In this study we have not considered the case of a blendstock that would require CN improver to meet the minimum CN requirements.

Prediction of Groundwater Contamination Potential

The potential for the release of a compound approved for use in fuel into the environment is significant. Groundwater contamination is likely for materials that are poorly biodegradable and have some solubility in water. While full assessment of the biodegradability is beyond the scope of Tier I and Tier II screening, a preliminary investigation of water solubility and anaerobic biodegradability using the U.S. Environmental Protection Agency's EPI Suite^{TM} Biowin7 model was performed. EPI Suite uses quantitative structure-activity relationship models to assess and predict the effect of chemical structure on the property of interest, which for this study is the biodegradation of the blendstock [28]. Biowin7 uses a linear fragment contribution model to assess anaerobic biodegradability. Thirty-seven unique chemical fragments from 169 training compounds were used to develop the model. More detail can be found in [29]. In our prior study of gasoline blendstocks [8], the criteria for groundwater contamination were to reject proposed blendstocks having water solubility and biodegradability greater than or equal to that of ethyl t-butyl ether. We have used the same criteria here.

Yield Sooting Index

The effect of a fuel blendstock on soot formation in MCCI combustion depends in a complex way on how blendstock physical properties affect the fuel spray, ignition delay, and the blendstocks' intrinsic sooting tendency [30]. For this assessment we report intrinsic sooting tendency of the blendstocks but do not apply it as a screening parameter. Yield sooting index is a measurement of a compound or fuel's chemical sooting tendency (independent of physical properties), acquired by measuring the yield of soot in a methane flame doped with a small amount of the test fuel. The method was originally developed using two different measurement scales for high sooting materials [31] and low sooting materials [32], but these have recently been harmonized with a unified YSI scale [9]. Das and coworkers also describe a modified Benson group-increment model to predict the YSI of a compound from its molecular structure that was used to predict YSI for compounds in this study for which a measured value was not available [9].

Lower Heating Value

Lower (or net) heating value (LHV) is obtained by subtracting the heat of vaporization of the water formed in combustion from the higher (or gross) heating value. In reporting LHV, it is assumed that water is in the vapor phase at the end of our combustion process and the heat of vaporization will not be recovered in a process that converts chemical energy as heat into work. As a measure of energy density, LHV on a mass or volumetric basis affects vehicle fuel economy (km/m^3 or mi/gal) and is thus a parameter of great practical and economic importance. LHV values are reported but were not used for blendstock screening. ASTM D240 was used to measure the LHV. Hydrogen content was calculated from molecular structure for pure components and measured using ASTM D5291 for mixtures.

FIGURE 1 Diagram of solubility sphere used to represent Hansen solubility parameters.

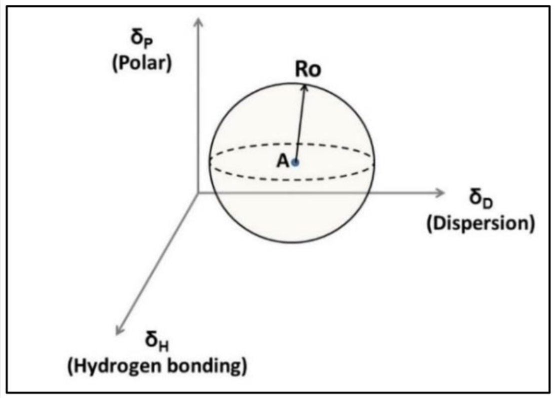

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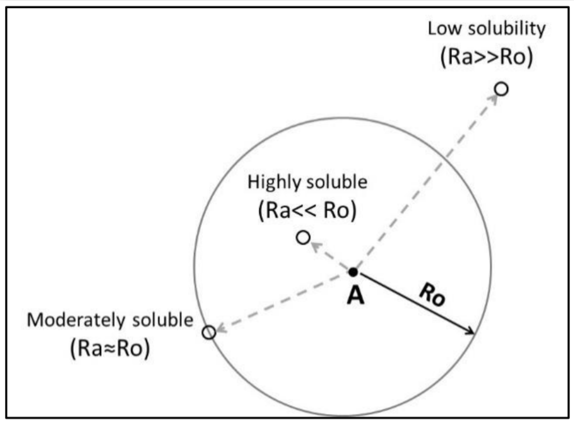
FIGURE 2 Two-dimensional representation of Hansen solubility sphere.



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Hansen Solubility Analysis to Assess Compatibility with Fuel System and Infrastructure Polymers

Elastomer compatibility of blends was assessed using solubility parameter theory. Solubility analysis is based on the weak binding forces that promote permeation and dissolution. Mutual solubility is based on the degree of similarity (affinity) of these binding forces that exist between the solute and solvent. In this study, the solutes are the solid elastomers and the solvents are the liquid fuel candidates, and their blends with diesel. Solubility analyses assign parameters to both the solute and solvent to represent these attractions, whereby solubility is proportional to the degree of similarity of these parameters to each other. For each material and fluid, the Hansen solubility parameter (HSP) method assigns a parameter to cohesive forces associated with atomic dispersion (δ_D), polarity (δ_P), and hydrogen bonding (δ_H) to represent the total cohesive energy density, which is the sum of the square of these three attractive forces as shown in equation 1 [33].

$$\delta_T^{\,2} = \delta_D^{\,2} + \delta_P^{\,2} + \delta_H^{\,2} \tag{1}$$

Compounds having similar HSPs will have similar attractive affinities. These three parameters define the location of a center of a sphere (labeled point A in Figure 1), the radius of which is known as the interaction radius (Ro). The interaction radius (Ro) is used as a fourth parameter in the Hansen method and is empirically determined (using a trial and error approach) as the boundary separating good and bad solvents [33]. Solvents having HSPs within this radius are considered good solvents, while solvents outside the boundary are less soluble and become more insoluble with increased distance as depicted graphically in the 2D schematic shown in Figure 1.

The similarity (or dissimilarity) is quantified by the differences between the HSPs for the solute and solvent. This difference is termed the solubility distance (Ra) and, for a polymer (p) and a liquid (l), is determined by equation 2:

$$Ra = \sqrt{\left[4\left(\delta_{D(p)} - \delta_{D(l)}\right)^2 + \left(\delta_{P(p)} - \delta_{P(l)}\right)^2 + \left(\delta_{H(p)} - \delta_{H(l)}\right)^2\right]} \tag{2}$$

As Ra decreases, the liquid becomes more soluble in the polymer, which correspondingly increases in volume. Figure 2 shows the location of three hypothetical Ra values relative to their location from the interaction radius. Fuels having solubility distance values much less than Ro would be considered highly soluble and could cause significant swell and potentially polymer degradation, while those having distances greater than Ro would have low solubility. Those lying on the surface of the sphere would be expected to exhibit modest to moderate solubility.

The difference between the solubility distance from the interaction radius (Ro – Ra) is roughly proportional to the predicted swell behavior of the polymer in the solvent (or fuel). A zero value occurs when the value of the solubility distance matches that of the interaction radius, while values less than zero become increasingly soluble. Likewise, values greater than zero become increasingly insoluble. A plot of Ro – Ra as a function of blend level is a useful means of assessing the relative solubility, and hence volume swell of a polymer.

Blend (Tier 2) Property Testing

Potential diesel blendstocks meeting the Tier 1 screening criteria were blended into a commercial diesel fuel at 20 vol-% for measurement of distillation (D86), carbon residue on the

10% bottoms (D524), cloud point (D5773), viscosity (D445), lubricity (D6079), conductivity (D2624), and oxidation stability (D7545). The purpose of these tests and the limits utilized for Tier 2 screening are shown in Table 2. Distillation is measured to reveal any non-ideal solution behavior (for example, the T50 depression observed for blends of ethanol into gasoline) and to confirm no negative impact on T90. The distillation 10% bottoms carbon residue is measured to determine if carbonaceous deposits could form from pyrolysis and polymerization of the blendstock at elevated temperatures. Cloud point measurement reveals if the blendstock is soluble in the fuel at low temperatures or otherwise would negatively impact cold temperature operation.

Lubricity is the ability of the fuel to provide lubrication and wear protection for fuel pumps and injectors. It is measured by rubbing two pieces of metal together while immersed in the fuel and measuring the wear scar produced during the test. A smaller wear scar indicates better lubricity, and the upper limit in the D975 standard for diesel fuel is 0.520 mm. Highly processed fuels such as ultra-low sulfur diesel can have very low electrical conductivity and can develop a static charge, which can result in a spark upon discharge. This presents a fire hazard during transport and handling of the fuel, which is mitigated by requiring a minimum electrical conductivity of 25 pS/m. Additives are very commonly used to improve lubricity and conductivity in conventional diesel fuels today. An untreated ultra-low sulfur diesel could exhibit a lubricity of 0.600 mm or higher or a conductivity as low as 1 pS/m.

Fuels can oxidize in storage to produce gums or other materials that can be harmful to engine fuel systems. While the ASTM D975 standard has no specific requirement for oxidation stability, the Top Tier diesel program requires a minimum 1 hr induction time on the D7545 test. Antioxidant additives are used to improve oxidation stability, most commonly with biodiesel blends. For blendstocks that failed the D7545 test, the test was repeated after treating with the common antioxidant butylated hydroxy toluene (BHT). Additionally, for a poorly stable ether blendstock, peroxide formation was monitored over 6 weeks of storage in air at 43°C (in line with the ASTM D4625 test for storage stability of distillate fuels). Peroxide concentration was measured following AOCS method Cd 8b-90, modified for potentiometric end point detection and smaller sample size.

The base diesel fuel used for blend preparation was acquired from a large commercial fuel distributor and determined to contain no biodiesel. The fuel was clay-treated to remove polar compounds such as additives that improve lubricity, conductivity, and oxidation stability to more accurately and objectively study the impact of the diesel blendstocks on these properties. Thus, the limits given for lubricity, conductivity, and oxidation stability in Table 2 are not used for eliminating blendstocks, as blends that fail these requirements can likely be modified to meet these specifications using additives as is commonly done for conventional diesel fuel today. The properties of the clay-treated diesel are shown in Table 3. Prior to clay treating, lubricity was 490 μm and conductivity was 110 pS/m, indicating that additives were removed by the clay treating. Blending was performed volumetrically.

TABLE 3 Composition and properties of clay-treated commercial diesel fuel used in blends for property measurements.

Property	ASTM Method	Units	Value
Flash Point	D93	°C	61
Water and Sediment	D2709	vol.-%	<0.005
Water	D6304	μg/g	37
Viscosity at 40°C	D445	cSt	2.663
Ash	D482	% mass	<0.001
Sulfur	D5453	μg/g	6.2
Copper Strip Corrosion	D130	N/A	1A
Aromatics	D1319	vol.-%	31.6
Cetane Number (ICN)	D8183	N/A	46.8
Distillation T90	D86	°C	330.2
Carbon Residue	D524	% mass	0.09
Lubricity	D6079	micron	520
Conductivity	D4308	pS/m	1
Oxidation Stability	D7545	minutes	68
Total Acid Number	D664	mg KOH/g	0.08
Peroxide Value	AOCS Cd 8b-90	mg/kg	1
Cloud Point	D5773	°C	-9.7

Cetane number (ICN by D8183) was measured for 10, 20, and 30 vol.-% percent blends into a seven-component surrogate diesel fuel. The seven-component diesel fuel was developed in collaboration with Lawrence Livermore National Laboratory. Composition and properties of the surrogate are shown in Table 4. This surrogate was designed to facilitate kinetic simulations of autoignition, and a detailed kinetic model is currently under development at Lawrence Livermore. Testing at three blend levels was conducted to determine if synergistic or antagonistic blending for CN occurred, as was observed in studies of effects on octane number for some gasoline blendstocks [8].

TABLE 4 Composition and properties of diesel seven-component surrogate used in blends for CN determination.

Composition	Molar %	Wt-%	Vol.-%
a-Methylnaphthalene	12.39	9.92	8.12
trans-Decalin	20.08	15.61	14.99
2,2,4,4,6,8,8-Heptamethylnonane	19.00	24.20	26.11
n-Butylcyclohexane	10.50	8.28	8.67
n-Hexadecane	16.61	21.15	22.89
Tetralin	13.78	10.25	8.83
n-Dodecylbenzene	7.64	10.59	10.39
Total	100.0	100.0	100.0
Average Molecular Weight	177.78		
Cetane Number (ICN D8183)	44.5		
Density, g/mL	0.8430		
Cloud point, °C	-10.5		

Results and Discussion

Screening of Blendstocks as Mixing Controlled Compression Ignition Engine Fuels

Out of 452 pure compounds and 4 mixture blendstocks in the database [10] at the time of analysis, 92 met the requirements for melting point, boiling point, water solubility, and flash point. A minimum CN of 40 was applied as an additional criterion, which reduced the number of candidates to 25. Of these 25, there were 10 pure compounds and 2 mixtures that were obtainable commercially or could be prepared in adequate quantity by biofuel production researchers. Table 5 lists the compounds and mixtures and their Tier I fuel property data. Table A.1 in the Appendix lists the additional compounds meeting the criteria that were not available for purchase or through synthetic routes and their measured or predicted Tier I properties. Of the 12 most promising bioblendstocks, there were five functional groups represented. It is notable that all blendstocks exhibit YSI values well below those of the primary soot-forming compounds in petroleum diesel [9].

Additionally, several potential blendstocks that have been researched extensively as diesel fuels were eliminated from consideration because of high water solubility. These are listed in Table A.2. These materials all have high oxygen content, which leads to low LHV. However, these glycol ethers and polymethylene ethers have also shown the potential for large soot reductions in MCCI combustion, and therefore might ultimately be of longer-term interest [34] [35] [36] [37]. They are not discussed further in this paper.

As discussed in our previous work [8], potential blendstocks were eliminated when two environmental fate conditions were met: poor anaerobic biodegradability and high water solubility greater than 10,000 mg/L. Inspection of water solubility values in Table 5 indicates that all blendstocks in the table exhibit water solubility well below this level; therefore, mobility in groundwater will be limited and the blendstocks are not likely of high concern for groundwater contamination. Nevertheless, it is notable that several of the blendstocks are unlikely to anaerobically biodegrade. Results from the Biowin7 model are reported in Table A.3 of the Appendix in terms of biodegradation probability. A probability above 0.5 indicates the compound is likely to biodegrade, while a value below 0.5 indicates biodegradability is not likely. Using this criterion, methyl decanoate is likely to anaerobically biodegrade, while 2-nonanol and hexyl hexanoate likely have some potential to biodegrade. The other compounds listed are not likely to degrade anaerobically. The next level screening (future work) will consider additional indicators of environmental fate, including fugacity, potential for bioaccumulation, and environmental partitioning.

Alcohols (1) Long-chain alcohols can be produced from long-chain fatty acids and triglycerides derived from biomass [38] or via microbial routes [39] However, the melting point of 1-decanol is 6°C, and values are even higher for longer chains (moving the alcohol group to an interior carbon atom lowers the melting point). Low-molecular-weight alcohols can have a low flashpoint, making them a safety issue for blends with diesel, and have a very low CN. Both flashpoint and CN increase with chain length, for example 1-octanol has a CN of 39 while 1-nonanol has a CN of 46 [40]. These facts significantly limit alcohols that could be used as an MCCI blendstock.

The single alcohol included in Table 5 is 2-nonanol, intended to be representative of alcohols with desirable MCCI fuel properties. It exhibits the minimum acceptable CN, but otherwise has excellent diesel properties. High viscosity may be an issue for long-chain alcohols; for example, 1-nonanol is predicted to have a viscosity of 11.5 cSt at 25°C [41] which is

TABLE 5 Compounds meeting Tier I requirements and their Tier I properties.

Name	CAS#	T_b (°C)	FP (°C)	T_m (°C)	ICN	Water sol, mg/L	YSI	LHV, MJ/L
2-Nonanol	628-99-9	193	96	-36	40	459.7*	52*	31.6
Butylcyclohexane	1678-93-9	181	50	-75	50	1.1*	77	35.5
2,6,10-Trimethyl Dodecane (farnesane)	3891-98-3	229	103	-73	59	0.004*	103*	33.7
n-Undecane	1120-21-4	196	65	-26	71	0.044	65	32.7
5-Ethyl-4-Propylnonane (80%)	53291-73-9	232	62	< -80	48	<0.1‡	99	34.3
Hexyl Hexanoate	6378-65-0	246	99	-55	40	3.52*	61*	30.2
Methyl Decanoate	110-42-9	224	111	-18	52	4.4	54*	29.6
Dibutoxymethane (DBM)	2568-90-3	179	62	-58	70	304.9*	45*	28.2
4-Butoxy Heptane (95%)	N/A	198	64	<-80	80	15‡	58	31.0
Dipentyl Ether	693-65-2	190	57	-69	111	27*	44	30.6
Mixtures:		T90 (°C)		CP (°C)				
Renewable Diesel	N/A	<338	>52	-6.5	80	<0.1	--	34.4
Soy Biodiesel	N/A	<360†	>93†	-0.6	52	<0.1	--	33.0

∗Predicted value. †As required by ASTM D6751, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels. ‡Measured, this study.

FP=flashpoint, CN= cetane number as indicated cetane number from D8183, CP=cloud point well above the range allowable for a finished diesel fuel. Notably, 1-octanol has been examined extensively as a diesel fuel component [42] and can be produced as a biofuel [43] however, its CN is below 40 and so was excluded based on our screening criteria.

Alkanes (5) Table 5 lists a linear alkane, a cycloalkane, two branched alkanes, and a mixture of predominantly isoalkanes (renewable diesel). Alkanes can be produced via biological [44] [45] [46] or by chemical and hybrid routes [47] [48].

While undecane and butylcyclohexane can be made by various routes, the other alkanes are products of specific processes. Farnesane (2,6,10-trimethyldodecane) is produced by hydrogenation of farnesene, which is produced via the isoprenoid metabolic pathway in a fermentation process [49]. The farnesane used was from a commercial producer. A C14 hydrocarbon 5-ethyl-4-propylnonane, was predicted to meet the requirements in Table 1 and was targeted for production by upgrading of butyric acid, which can be produced from anaerobic fermentation of lignocellulosic sugars [50]. This upgrading occurs through sequential ketonization, condensation, and hydrodeoxygenation reactions. Due to limited availability of this alkane from a commercial source, we examined a hydrocarbon mixture derived from upgrading of commercial 4-heptanone, which is the major product from C4 acid ketonization. This product consists of approximately 80% 5-ethyl-4-propylnonane and other hydrocarbons, including heptane, C14 hydrocarbon isomers, and unidentified non-cyclic and cyclic hydrocarbons [51]. Renewable diesel is a commercial biofuel produced by hydroprocessing of esters and fatty acids [52] and was acquired from the producer.

These alkanes generally have excellent diesel fuel properties as neat blendstocks with values typically well beyond the minimum requirements. The relatively high YSIs of farnesane and 5-ethyl-4-propylnonane are notable, but these values are still well below that of common petroleum diesel components that contain an aromatic ring [9].

Esters (3) Methyl esters are the primary components of biodiesel, a commercial biofuel, and one of the blendstocks listed in Table 5. Biodiesel is the largest volume commercially produced form of biomass-based diesel globally [53] and has well-established ASTM requirements for the 100% biodiesel blendstock as well as for blends with petroleum fuels. The soy biodiesel used here was acquired from the producer and met all requirements of the ASTM D6751 standard. Methyl decanoate is a similar methyl ester and potentially a major component of biodiesel produced from some oils [54], but can also be produced from decanoic acid obtained by other means [55]. Hexyl hexanoate is produced by esterification of hexanoic acid with 1-hexyl alcohol. This idea was first proposed for pentanoic acid, which is produced from levulinic acid by hydrogenation [56]. Half of the acid is converted to 1-pentanol, and the acid and alcohol are combined to produce the ester. Hexanoic acid can be produced by fermentation of sugars [57], and conversion to hexyl hexanoate by a similar route may be an approach to utilization of this product as a biofuel. Soy biodiesel has a cloud point that is only slightly below the maximum allowed by our screening criteria, but nevertheless is used on a large scale. Other fuel properties of the esters are inside the desired range.

Ethers (3) Three ethers were identified as having suitable properties for use as an MCCI fuel. Dibutoxymethane (DBM) can be prepared from fermentation-derived 1-butanol [58] by reaction with formaldehyde [59]. DBM has been examined as a diesel blendstock and shown to produce substantial reductions in particle emissions, [60]. Extensive data on the properties of DBM blended with diesel have been presented in [61]. The C11 ether 4-butoxy heptane was selected based on predicted fuel properties and can be produced from fermentation-derived butyric acid [50]. This requires dividing the butyric acid into two separate streams, one to ketonize the butyric acid to 4-heptanone and the other to reduce it to n-butanol. Due to limited availability of this ether from commercial source, we examined the ether derived from the catalytic upgrading of commercial 4-heptanone and 1-butanol that resulted in a mixture of over 95% target 4-butoxyheptane with the balance composed of trace amounts of 4-heptanone, n-butyl ether, and 4-heptanol [62]. Dipentyl ether can be produced from 1-pentanol, which is straightforward to produce from biomass-derived sugar. [56] Data on the properties of dipentyl ether blends in diesel have been presented in [61], confirming its notably high CN.

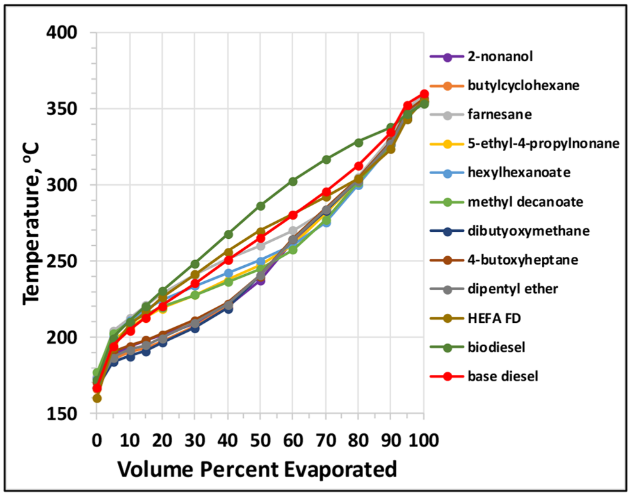
Properties of Blends with Conventional Diesel

The 12 blendstocks listed in Table 5 were used to prepare several blends in a clay-treated diesel or a seven-component surrogate to evaluate their Tier II properties. Blends were prepared at a 20% blend level in the clay-treated diesel to assess their effect on cloud point, flash point, oxidation stability, lubricity, pour point, conductivity, and viscosity. Carbon residue was measured on the 10% bottoms sample. The 12 candidates were also blended at 10%, 20%, and 30% in the seven-component surrogate, and the ICN was measured. Table 6 shows the fuel property measurement results of the 20% blends in the clay-treated diesel.

As can be seen in Table 6, the blends generally had lower or similar cloud points as the base diesel. In most cases, blending slightly reduced viscosity, the exceptions being farnesane and 2-nonanol, which showed a slight increase. However, all samples were within the upper and lower limits for kinematic viscosity in the D975 standard. The blendstocks all boiled well below the T90 of the base diesel and had minimal effect on T90. The exception was biodiesel; however, the T90 value was below the maximum allowed (343°C) in ASTM D7467, Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20). There was also no significant effect on distillation bottoms carbon residue for any of the samples.

Figure 3 displays the D86 distillation data for 20% blends into the clay-treated diesel. Tabulated D86 data are shown in Table A.4 in the Appendix. Undecane, 2-nonanol, butyl cyclohexane, dipentyl ether, 4-butoxy heptane, and DBM showed a depression in the D86 curve, especially in the 10%-50% fraction evaporated region compared to the clay-treated diesel. This may be advantageous for increasing the premixed burn

FIGURE 3 D86 results of 20% blends in clay-treated diesel.



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fraction in diesel combustion, which may lead to improved combustion efficiency [4]. Methyl decanoate, hexyl hexanoate, 5-ethyl-propyl nonane, and farnesane did not significantly affect the distillation curve of the base diesel. Soy biodiesel showed an increase in the temperatures across the distillation curve when blended into the clay-treated diesel.

Figure 4 shows conductivity and lubricity data for the 20% blends graphically. Renewable diesel and 2-nonanol increased the conductivity to above the minimum requirement of 25 pS/m. As a commercial fuel blendstock, it is likely that the renewable diesel sample had been treated with a conductivity improver additive. While the other blendstocks did not increase the conductivity significantly, a conductivity additive could be used to increase the conductivity to an acceptable level. Farnesane and soy biodiesel showed the largest impact on lubricity, with hexyl hexanoate and methyl decanoate improving lubricity slightly. Because the farnesane was a commercially produced fuel, it may have contained a lubricity improver

FIGURE 4 Conductivity and lubricity results for 20% blends in clay-treated diesel. Yellow line denotes minimum required level in D975 for conductivity and maximum allowed level in D975 for wear scar diameter.

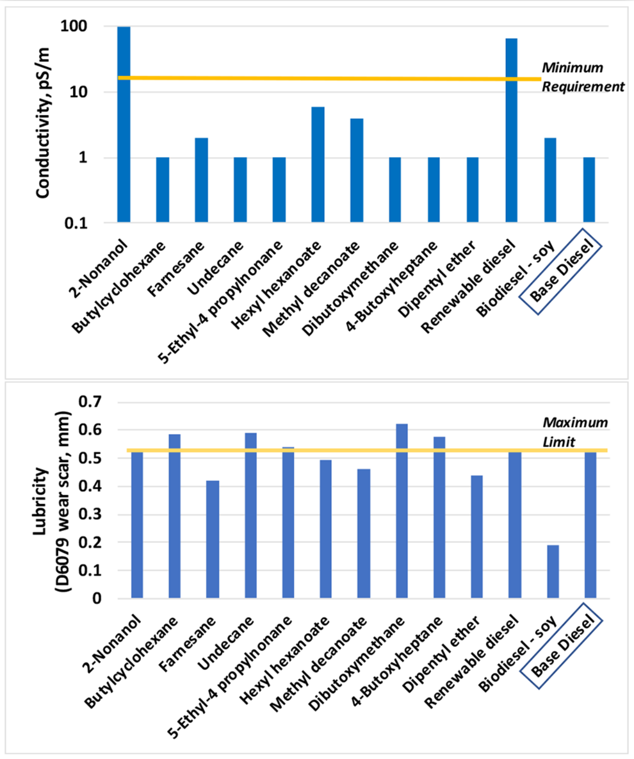

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TABLE 6 Tier II testing results for 20% blends in clay-treated diesel.

Name	CP (°C)	Viscosity (cSt at 40°C)	Distillation T90 (°C)	Carbon Residue 10% bottoms (wt-%)	Lubricity (mm)	Conductivity (pS/m)	Oxidation Stability (min)
2-Nonanol	-10.1	2.766	327	0.10	0.526	100	126
Butylcyclohexane	-13.3	2.194	327	0.09	0.584	<1	62.0
2,6,10-Trimethyl dodecane (farnesane)	-11.7	2.819	331	0.13	0.418	2	57.4
n-Undecane	-12.7	2.170	327	0	0.590	<1	99.6
5-Ethyl-4-propylnonane (80%)	-11.2	2.378	327	...	0.538	1	76.6
Hexyl hexanoate	-10.9	2.375	326	0.09	0.493	6	120
Methyl decanoate	-11.4	2.325	326	0.09	0.462	4	95.5
Dibutoxymethane (DBM)	-12.1	2.014	328	0.08	0.622	<1	74.3
4-Butoxy heptane (90%)	-11.4	2.119	329	0.06	0.578	1	23.2
Dipentyl ether	-12.0	2.124	327	0.10	0.437	<1	55.9
Renewable diesel	-11.9	2.664	324	0.09	0.524	66	72.8
Soy biodiesel	-9.2	2.385	338	0.07	0.189	2	40.4
Base Diesel (clay treated)	-9.7	2.663	335	0.09	0.520	1	69.6

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additive. Biodiesel is well known to improve lubricity because both the ester group and common impurities have lubricity properties [63]. The other esters are reagent chemicals without impurities, accounting for their reduced impact on lubricity.

Oxidation stability induction times measured for the 20% blends using method D7545 are reported in Figure 5. For oxidation stability, some blendstocks increased stability significantly, for example, 2-nonanol, undecane, hexyl hexanoate, and methyl decanoate, while others had only a small effect. Two exceptions are soy biodiesel and 4-butoxy heptane, which both significantly reduced stability relative to the starting diesel. The soy biodiesel had a stability value of over 6 hr, easily meeting the minimum stability requirement of 3 hr on the EN15751 test as required by its blendstock ASTM standard (D6751). This blendstock likely had the opposite effect of the other esters considered here because it contains predominantly unsaturated fatty acid chains while hexyl hexanoate and methyl decanoate are fully saturated. These results indicate that additional antioxidant additive is required for this 20% biodiesel blend to meet the Top Tier diesel requirement of 60 min on the D7545 test. Biodiesel is commonly treated with antioxidants to ensure stability in the commercial market [64].

The ether 4-butoxyheptane oxidized rapidly in this test, and in addition was shown to have oxidized to form high levels of peroxides over 6 weeks at 43°C under conditions similar to those of the ASTM D4625 long-term storage test. These results are shown in Table A.6 of the Appendix, along with results for isoamyl ether for comparison. Isoamyl ether formed a factor of 100 lower peroxides than 4-butoxyheptane. The structure of 4-butoxyheptane likely lends itself to the production of a stable radical, which allows for relatively rapid autoxidation. Stabilizing the pure ether with 100 ppm of BHT, or a 20% blend with the clay treated diesel with 20 ppm of BHT, was highly effective at preventing oxidation (Table A.6).

Figure 6 shows the CN data for the 10%, 20%, and 30% blends in the seven-component surrogate. (Note that inadequate sample was available to test 5-ethyl-4-propyl nonane). The tabulated data are included in Table A.5 in the Appendix. These results are consistent with linear blending for CN; however, examination of blending CN suggests a more complex picture. Volumetric blending cetane number (bCNv) was calculated at each blend level using equation 3.

FIGURE 5 Oxidation stability for the 20% clay treated diesel blends as measured by the ASTM D7545 test. Note that the minimum induction time requirement for Top Tier diesel is shown.

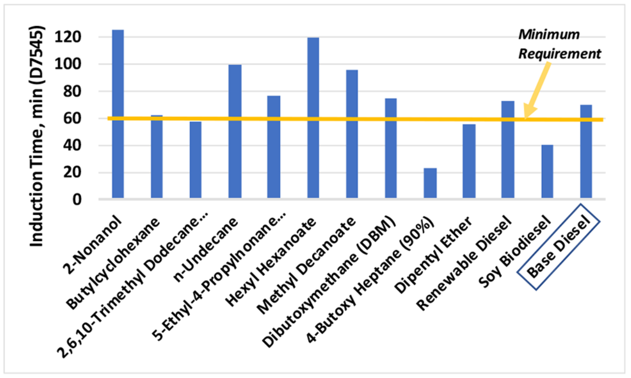

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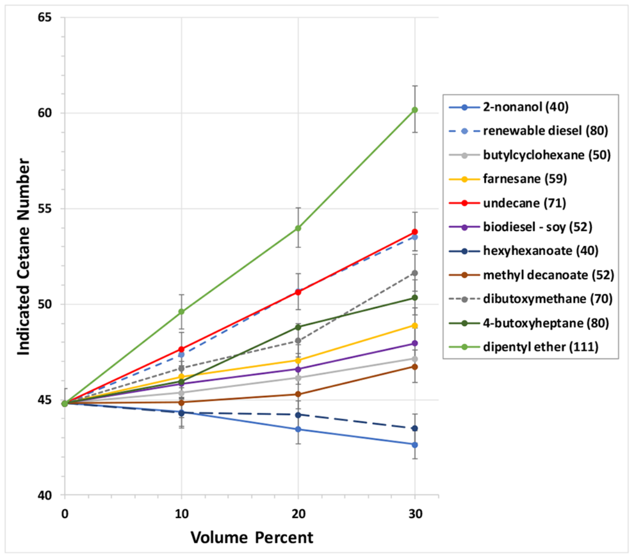
FIGURE 6 CN data (ICN by D8183) for 10%, 20%, and 30% blends of Tier I bioblendstocks into the seven-component surrogate. Values in legend are neat blendstock CN.



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$$\mathrm{bCNv} = \left[\mathrm{Blend\ CN} - \mathrm{Vs}^{*}\mathrm{CNs}\right]/\mathrm{Vb} \tag{3}$$

where:

Blend CN = CN of the surrogate+blendstock blends
CNs = CN of surrogate
Vs = volume fraction of surrogate
Vb = volume fraction of blendstock

These results are plotted in Figure 7. Many blendstocks blended linearly, that is, the calculated bCNv is similar to the pure component value. In a few instances we observe antagonistic blending-the bCNv is lower than the pure component value (dipentyl ether, renewable diesel, DBM at 10% and 20%, 4-butoxy heptane, and methyl decanoate at 10% and 20%). We speculate that in antagonistic blending for CN, the surrogate interferes with the autoignition of the high-CN blendstock, acting as a radical scavenger and reducing the increased rate of autoignition expected based on a linear model. As the concentration of the blendstock increases, it is ultimately able to overwhelm the impact of the surrogate; hence, we see increasing bCNv with increasing blend level. Additional research is needed to more fully understand the chemical kinetic interactions that lead to antagonistic blending.

Solubility Parameter Analysis of Compatibility with Fuel System and Infrastructure Elastomers and Plastics

Hansen solubility analysis was performed on 11 of the MCCI blendstock candidates as a function of blend level with diesel fuel. The solubility parameters are listed in Table 7 for each

FIGURE 7 Volumetric blending cetane number (bCNv) for 10%, 20%, and 30% blends and neat component CN for the Tier 1 blendstocks.

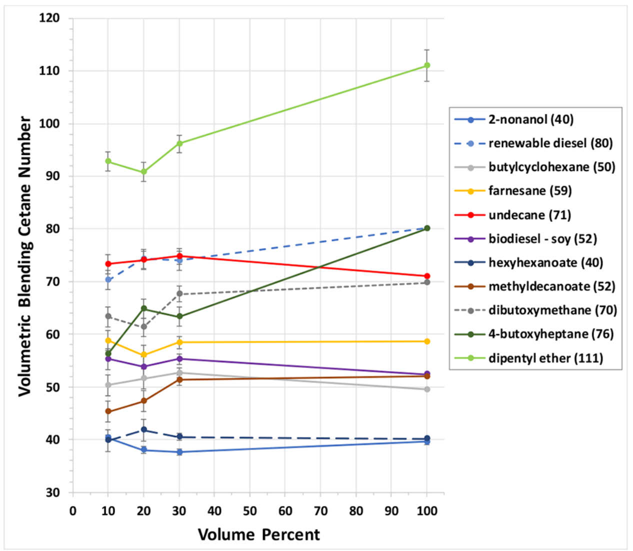

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TABLE 7 HSPs for each pure component MCCI blend.

Class	MCCI Candidate	Hansen Solubility Parameters (MPa$^{1/2}$) δ_D	δ_P	δ_H	Source
Alcohols	2-Nonanol	16.1	4.2	8.2	HSPiP Database
Alkanes	Butylcyclo-hexane	16.2	0	0.6	HSPiP Database
	2,6,10-Trimethyl dodecane	15.6	0.1	0.1	HSPiP Database
	5-Ethyl-4 propyl nonane	15.6	0.1	0.1	Calc. using HSPiP tool
	n-Undecane	16.0	0.0	0.0	HSPiP Database
Esters	Hexyl hexanoate	16.1	3.1	4.1	HSPiP Database
	Methyl decanoate	16.1	3.2	4.3	HSPiP Database
Ethers	DBM	15.7	4.2	4.0	Calc. using HSPiP tool
	Dipentyl ether	15.6	3.1	3.0	HSPiP Database
	4-Butoxy heptane	15.6	2.2	2.3	Calc. using HSPiP tool
Diesel		17.0	2.0	2.0	Steve Abbott (HSPiP Database Manager) [66]

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candidate along with diesel. As shown in the table, the parameters for many of the candidates were listed in the HSPiP database [65], but three of the alkanes were not. The parameters for 5-ethyl-4 propylnonane, DBM, and 4-butoxy heptane were calculated using the algorithm tool in the HSPiP software [65].

As can be seen in the table, the parameters are generally similar for the candidates within each class of compounds, which is to be expected given the similarities of the molecular structures. For each of the candidates, the dispersion forces are roughly similar. The alcohol candidate shows high hydrogen bonding and moderate polarity. In contrast, the alkane candidates exhibit low polarity and hydrogen bonding. The alkanes 2,6,10-trimethyldodecane and 5-ethyl-4-propylnonane have identical HSPs and therefore will produce identical results in the analysis. While the renewable diesel was not considered in the HSP analysis because it consists primarily of isoalkanes, its performance should be very similar to that of the pure component alkanes listed here. The two ester molecules have nearly identical HSPs and therefore would be expected to exhibit similar compatibility performance. These HSP values are similar to those reported in the literature for the different fatty acid methyl esters comprising biodiesel [67] The three ethers exhibit notable differences, especially in polarity and hydrogen bonding. HSPs for the diesel-blendstock blends were calculated as a volume weighted average.

Table 8 lists HSPs for 12 critical fuel system and infrastructure elastomers and plastics along with their applications. The elastomers are used primarily as seals and as flexible hoses, while many of the plastics are used as seals, liners, and structural components. Obtaining accurate HSPs for polymers is challenging because HSPs have been determined for only a limited number of grades, and the composition can vary significantly depending on the manufacturer. This difficulty is compounded by the lack of compositional data, which is considered proprietary by most manufacturers. In many instances, the HSPs provided in the literature have questionable accuracy. Nevertheless, the HSPs listed in Table 8 have been shown to correspond well to the relative measured swell [67] [68] [69]. For the polymers an additional parameter, the interaction radius, is also listed. This radius defines the solubility sphere for each polymer.

Many of the polymers listed in Table 8 show high polarity and hydrogen bonding and therefore would be expected to show increased solubility, and hence swell, with those MCCI candidates having similarly high polarity and hydrogen bonding. The HSPs listed in Table 8 were derived from the HSPiP dataset. However, because no HSPs were listed for fluorosilicones in the literature, they were calculated based on 2,4,6-trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)-1,3,5,2,4,6-trioxatrisilinane, which forms the base molecular structure for fluorosilicone. The interaction radius was derived using a trial-and-error approach using volume swell measurements from previous studies [68, 70, 71, 69, 72, 67]. It is important to note that the two NBR grades have differing parameters (especially polarity). This difference reflects the wide range of engineered properties that are achieved with NBR. While the HSP approach is good at predicting relative swell of NBRs in gasoline and alcohols, it is less accurate for diesel. This is attributed to the wide variability in performance of NBRs, and that the HSPs used in solubility analyses are not precise representatives of the grades evaluated in the exposure studies. Both HYCAR 1052 and Buna-N grades are reported to be compatible with fuel oils and as such are considered relevant for applications with MCCI blendstocks.

TABLE 8 Selected fuel system polymers and the HSPs used in this study [33, 65].

	Hansen Solubility Parameter ($MPa^{1/2}$)				
Polymer Type	δ_D	δ_P	δ_H	Ro	**Application**
Elastomers					
Fluoroelastomer (Viton™)	14.6	10.0	1.6	8.8	Seals, liners, hoses
Fluorosilicone	11.2	2.3	0.1	9.0	Seals
Neoprene	18.1	14.3	6.7	8.9	Seals and hoses
Epichlorohydrin rubber	21.3	8.1	6.1	12.0	Legacy seal material
NBR (HYCAR 1052)	18.6	8.8	4.2	9.6	Seals and hoses
NBR (Buna-N)	17.8	3.2	3.4	3.7	Seals and hoses
Plastics					
Polytetrafluoroethylene (PTFE) or Teflon™	17.1	8.1	1.3	4.7	Liners and seals
Polyvinylidene fluoride (PVDF)	17.0	12.1	10.2	8.0	Plastic piping
Nylon 66 (PA 66)	18.2	8.8	10.8	5.2	Plastic piping and seals
Nylon 12	18.5	8.1	9.1	6.3	Fuel lines and plastic piping material
High Density Polyethylene (HDPE)	18.0	0.0	2.0	2.0	Fuel tanks
Polyoxymethylene (POM) or acetal	17.2	9.0	9.8	5.3	Fuel line valves, pump and tank components

The solubility results for the MCCI blend stocks are shown in Figures A.1-A.6 for the elastomers and in Figures A.7-A.12 for the plastics in the Appendix. For each material and fuel type, Ro − Ra was plotted as a function of blend level with diesel. Values of Ro − Ra that are less than zero (which corresponds to the surface of the solubility sphere) are viewed as likely compatible based on previous studies comparing volume swell with solubility. Values between 1 and 2 $MPa^{1/2}$ are likely compatible for sealing applications. However, the confidence is not high since moderate swelling may not be suitable for use as a dynamic seal. Ro − Ra values higher than 2 $MPa^{1/2}$ are likely incompatible for most applications. It is important to note that acceptability is highly dependent on the application. Many of the plastics are used as structural components, which cannot tolerate moderate levels of swell. For these materials, Ro − Ra values exceeding zero are of concern. The uncertainty associated with solubility analyses necessitates experimental studies prior to use. However, the analyses are useful for identifying potential incompatibilities and understanding the impact of blend levels.

The alcohol 2-nonanol appreciably raised the solubility of diesel blends with fluorocarbon, NBR, neoprene, PVDF, POM, and the two nylon grades. For the other polymers, solubility was unchanged or declined with the addition of the alcohol blend stock molecules. The maximum solubility values for fluorocarbon are low for a seal material, and prior studies have shown fluorocarbon to be highly compatible with alcohols. The solubilities of the two NBR grades were enhanced at low blend levels, and further studies are recommended to determine the suitability of long-chain alcohols with components composed of NBR. A more dramatic increase in solubility was noted for neoprene. Neoprene would not be recommended for use with 2-nonanol or other long-chain alcohols unless deemed compatible in an exposure study.

The four alkane molecules butylcyclohexane, 2,6,10-trimethyldodecane, n-undecane, and 5-ethyl-4 propylnonane performed similarly to each other as expected. These fuels produced decreasing solubility with blend level for each polymer type, except fluorosilicone. Even for fluorosilicone, the increase in solubility accompanying alkane blends was too low to be of concern.

The two ester molecules, hexyl hexanoate and methyl decanoate, did not produce any notable increases in solubility with either the elastomer or plastic materials. In most cases, the solubility was relatively unaffected or was observed to increase or decrease moderately with blend content. The largest increase in solubility occurred for fluorosilicone, but even here the values are considered too low to be of concern. In summary, the analysis suggests that the ester blend stocks should be compatible with fuel system polymers. Notably, biodiesel in 100% form is not considered to be compatible with NBR or neoprene; however, these effects may be insignificant at lower blend levels [73].

Dipentyl ether showed good compatibility (low solubility) with each of the elastomer and plastic materials. 4-Butoxy heptane also showed decreasing solubility with blend level. DBM tended to have more variable behavior with the polymers. However, DBM did not produce high solubilities in any of the elastomers or plastics evaluated in this study that would be a compatibility concern.

In summary, the blendstocks listed in Table 6 are predicted to be compatible with the elastomers listed in Table 8 at all blend levels, with the exception that long-chain alcohols are likely incompatible with neoprene and should be evaluated experimentally before using with various NBR grades.

Summary/Conclusions

An approach for a fuel property-based screening of potential MCCI blendstocks was developed and presented. Over 400 blendstocks were screened for basic MCCI blendstock properties. This led to a list of 25 that met all property requirements of which 12 could be obtained for experimental research and property validation. These included a long-chain alcohol, five alkanes, three esters (including biodiesel), and three ethers. These were blended into a clay-treated diesel to access their effect in blends at a 20% blend level. Blends of 10%, 20%, and 30% in a seven-component surrogate were also prepared, and CN (as ICN) was measured for these samples.

Examination of fuel properties during screening shows that primary or secondary alcohols must be in approximately the C9 to C10 molecular weight range as smaller molecules have low cetane number and flashpoint while larger molecules are likely to have too high a melting point. Additional research is required to determine if the viscosity of long-chain alcohols is too high for practical commercial application. As expected, alkanes in the diesel boiling range, including normal, iso-, and cyclo-alkanes exhibited good properties as diesel blendstocks. This includes the commercial biofuel known as renewable diesel that is produced by hydroprocessing of esters and fatty acids. Properties of the esters examined were well inside the desired range for MCCI blendstocks. Because of its relatively high degree of unsaturation, soy biodiesel may not meet the Top Tier diesel oxidation stability requirement unless adequately treated with antioxidant additive (a fact well appreciated in the commercial fuel market). Ether blendstocks also showed excellent MCCI blendstock properties. However, 4-butoxy heptane appeared highly susceptible to peroxide formation and exhibited poor oxidation stability. This is in contrast with results for the other ethers, dibutoxymethane and dipentyl ether, which were more stable. Additional research is needed to understand specific structural features of ethers that can lead to poor stability. However, 4-butoxyheptane appeared to be easily stabilized using the common antioxidant BHT.

Most of the blendstocks would likely require the use of lubricity and conductivity improver additives to meet finished fuel requirements in blends with conventional diesel. While most blendstocks exhibited linear blending (on a volumetric basis) for CN, dipentyl ether, renewable diesel, DBM at 10% and 20%, 4-butoxy heptane, and methyl decanoate at 10% and 20% showed non-linear, antagonistic blending. This means that their volumetric blending CN was significantly lower than their pure component CN. We propose that the surrogate interferes with the autoignition of the high-CN blendstocks, acting as a radical scavenger and reducing the increased rate of autoignition expected based on a linear model. As the concentration of the blendstock increases, it is ultimately able to overwhelm the impact of the surrogate; hence, we see increasing volumetric blending CN with increasing blend level. Additional research to understand the molecular-level interactions responsible for antagonistic blending is needed.

A Hansen solubility analysis indicates that the alkanes, esters, and dipentyl ether blendstock molecules will likely be compatible with critical fuel system polymers. The alcohol candidate 2-nonanol shows high solubilities with neoprene and potentially with nitrile butadiene rubber polymers at low blend levels. The implication is that this molecule may not be suitable for use in some fuel systems. Further evaluations based on exposure studies and volume swell and hardness measurements need to be conducted on these mixing controlled compression ignition candidates to confirm performances and determine infrastructure compatibility.

Results suggest that all 12 blendstocks have reasonable potential as commercial diesel fuels based on fuel properties. Based on their low yield sooting index values, they might all be expected to reduce particulate matter emissions from diesel combustion - however CN and fuel physical properties including viscosity, density, and surface tension will also play a role. Future work under the Co-Optima project will examine many of these blendstocks in engine combustion experiments.

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Definitions/Abbreviations

ASTM - ASTM International
bCNv - volumetric blending cetane number
BHT - butylated hydroxy toluene
CN - cetane number
Co-Optima - Co-Optimization of Fuels & Engines
CP - cloud point
DBM - dibutoxymethane
FP - flashpoint
HDPE - high-density polyethylene
HSP - Hansen solubility parameter
ICN - indicated cetane number
LHV - lower heating value
MCCI - mixing controlled compression ignition
NBR - nitrile butadiene rubber
OSHA - Occupational Safety and Health Administration
POM - polyoxymethylene
TAN - total acid number
$\mathbf{T_b}$ - boiling point
$\mathbf{T_m}$ - melting point
TPGME - tripropylene glycol monomethyl ether
Vb - volume fraction of blendstock
Vs - volume fraction of surrogate
YSI - yield sooting index

Appendix

TABLE A.1 Additional bioblendstocks meeting Tier I criteria that were not commercially or synthetically available.

Compound	CAS#	FP (°C)	MP (°C)	BP (°C)	CN	Water Solubility (mg/L)	Probability of Anaerobic Biodegradation by Biowin7
Octadeca-6,9-diene	6114-20-1	145.1P	-45.0	307	91.3P	Not available	Not available
3-Undecene	1002-68-2	59.8P	-62.1	194	57.7P	0.401	0.764
1-Ethoxy-3,7-dimethyl-2,6-octadiene	40267-72-9	86P	-22.6P	218	68.3P	5.618	0.2175
2,7-Dimethyl-nonane	17302-29-3	109P	-54.8P	182P	55.1P	0.343	Not available
2,4,6-Trimethyl-octane	62016-37-9	52.7P	-66.1P	169	41P	0.397	0.0186
Tridecane	629-50-5	94.0	-5.3	235	89.5	0.027	0.3274
1-Methyl-2 pentylcyclopentane, cis-	53366-47-5	61.5P	-28.7P	187P	60.1P	0.437	Not available
4-Nonanone	4485-09-0	61	-19	188	43	284.4	0.1233
3,7,11-Trimethyl-3-dodecanol	7278-65-1	116.8P	-69.6	273P	59.9	0.774	-0.0458

P=predicted

TABLE A.2 Additional bioblendstocks meeting screening requirements except for water solubility

Compound	CAS#	FP (°C)	MP (°C)	BP (°C)	CN	Water Solubility (mg/L)	Probability of Anaerobic Biodegradation by Biowin7
Diethylene glycol monoethyl ether (DGME)	111-90-0	96	-80	202	55	82,800P	0.5047
Tripropylene glycol monomethyl ether (TPGME)	25498-49-1	113	-42	262	58	Highly soluble	-0.5408
2,4,6,8-Tetraoxanonane	13353-03-2	54.0	-43.0	156	70.0	1,000,000	NA
2,4,6,8,10- Pentaoxaundecane	13352-75-5	88.0	-10.0	201	90.0	1,000,000	NA
3,5,7,9-Tetraoxaundecane	4431-82-7	68.0	-24.0	185	67.0	Not Available but likely highly soluble	NA

P=predicted

TABLE A.3 Anaerobic biodegradation potential calculated using Biowin7.

Name	Probability of Rapid Biodegradation, Biowin7
2-Nonanol	0.4821
Butylcyclohexane	-0.0439
2,6,10-Trimethyl dodecane (farnesane)	0.1226
n-Undecane	0.2754
5-Ethyl-4-propylnonane (80%)	0.0763
Hexyl hexanoate	0.4472
Methyl decanoate	0.7390
Dibutoxymethane (DBM)	-0.2911
4-Butoxy heptane (95%)	0.0385
Dipentyl ether	-0.0078

TABLE A.4 Tabulated D86 data for 20% blends of bioblendstocks in clay-treated diesel.

	Temperature (°C)				
Fraction Evaporated	**20% Soy Biodiesel**	**20% Farnesane**	**20% 2-Nonanol**	**20% Undecane**	**20% Butyl Cyclohexane**
0	171.8	174.4	174.1	169.4	166.3
5	199.2	204.1	188.9	190.8	185.1
10	210.2	212.7	193.5	195.8	189.8
15	220.7	220.9	197.6	200.3	193.2
20	230.3	228.0	201.0	204.6	197.2
30	248.5	240.9	209.2	213.1	206.9
40	267.7	251.2	219.8	224.3	219.8
50	286.4	260.1	237.3	238.6	239.9
60	302.8	270.0	262.8	261.6	262.8
70	316.8	282.7	282.1	282.7	283.5
80	328.3	304.9	302.4	302.7	303.4
90	338.0	330.8	326.7	326.7	327.4
95	346.6	349.7	344.1	344.4	345.7
100	353.3	358.8	355.1	354.3	355.3

	Temperature (°C)				
Fraction Evaporated	**20% Dibutoxymethane**	**20% Hexyl Hexanoate**	**20% Methyl Decanoate**	**20% 1-Octanol**	**Clay-Treated Diesel**
0	166.6	173.2	176.9	173.9	166.9
5	183.8	201.2	202.2	187.2	194.1
10	187.6	210.8	210.0	191.2	204.6
15	190.9	217.9	215.1	194.0	212.8
20	196.2	223.8	219.6	197.2	220.4
30	205.9	233.8	227.8	205.0	235.6
40	218.8	242.0	236.1	217.6	250.6
50	240.0	250.1	244.8	243.1	265.3
60	264.1	260.3	257.4	268.3	280.3
70	282.9	275.4	276.9	286.6	295.8
80	303.2	299.9	301.4	306.3	312.6
90	327.5	326.3	326.1	330.0	334.6
95	345.4	343.7	344.0	347.7	353.0
100	355.3	354.9	354.8	357.3	360.1

TABLE A.5 ICN data for 10%, 20%, and 30% blends of Tier I blendstocks in 7-component surrogate.

Blend ID	Average ICN
Base 7-Component Surrogate	44.8
10% 1-Nonanol	44.4
20% 1-Nonanol	43.5
30% 1-Nonanol	42.7
1-Nonanol	39.6
10% 1-Octanol	43.9
20% 1-Octanol	43.6
30% 1-Octanol	42.7
1-Octanol	37.6
10% Butylcyclohexane	45.4
20% Butylcyclohexane	46.2
30% Butylcyclohexane	47.2
Butyl cyclohexane	47.6

TABLE A.5 (Continued) ICN data for 10%, 20%, and 30% blends of Tier I blendstocks in 7-component surrogate.

Blend ID	Average ICN
10% Farnesane	46.2
20% Farnesane	47.1
30% Farnesane	48.9
Farnesane	58.6
10% Undecane	47.7
20% Undecane	50.7
30% Undecane	53.8
Undecane	83.0
10% Decane	47.1
20% Decane	50.7
30% Decane	52.8
Decane	66.0
10% hexyl hexanoate	44.3
20% hexyl hexanoate	44.2
30% hexyl hexanoate	43.5
Hexyl hexanoate	40.2
10% methyl decanoate	44.9
20% methyl decanoate	45.3
30% methyl decanoate	46.8
Methyl decanoate	52.0
10% Dibutoxymethane	46.7
20% Dibutoxymethane	48.1
30% Dibutoxymethane	51.7
Dibutoxymethane	67.0
10% TPGME	45.1
20% TPGME	46.5
30% TPGME	47.4
TPGME	65.0
10% Clay-Treated Diesel	45.9
20% clay-treated diesel	46.6
30% clay-treated diesel	48.0
Clay-treated diesel	52.4
10% ether combo	46.0
20% ether combo	50.4
Ether combo	76.0
10% renewable diesel	47.4
20% renewable diesel	50.7
30% renewable diesel	53.6
Renewable diesel	80.1

TABLE A.6 Peroxide value results during aging of 4-butoxyheptane and isoamyl ether under conditions similar to the ASTM D4625 test (43°C). Data scatter for the BHT treated samples is due to values being near the blank value - these are essentially at the limit of detection but below limit of quantitation.

ppm (mg/kg) Peroxide	Isoamyl Ether	4-Butoxyheptane	4-Butoxyheptane + 100 ppm BHT	20 vol-% 4-Butoxyheptane in clay treated diesel + 20 ppm BHT
Initial	4.0	14.7	0.7	0.8
2 weeks	6.1	35.3	2.5	2.5
4 weeks	7.2	1088	0.5	0.5
6 weeks	14.5	3013	0.8	1.6

FIGURE A.1 Solubility curves for fluorocarbon (Viton™) for each of the MCCI fuel candidates as a function of blend level in diesel.

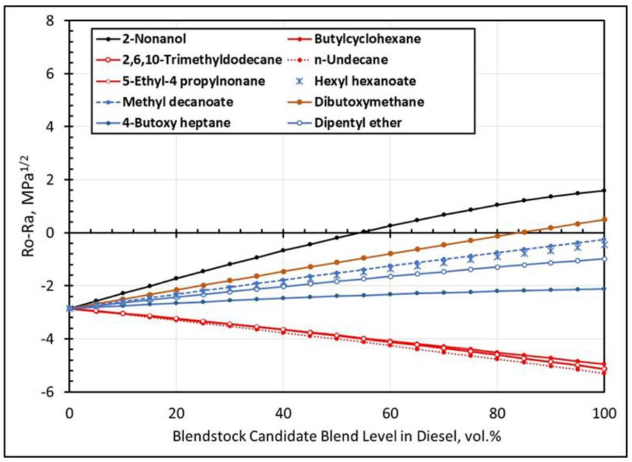

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FIGURE A.2 Solubility curves for fluorosilicone for each of the MCCI fuel candidates as a function of blend level in diesel.

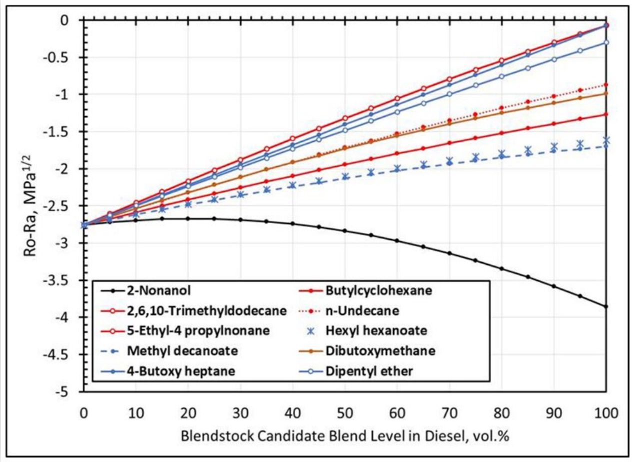

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FIGURE A.3 Solubility curves for NBR (HYCAR 1052) for each of the MCCI fuel candidates as a function of blend level in diesel.

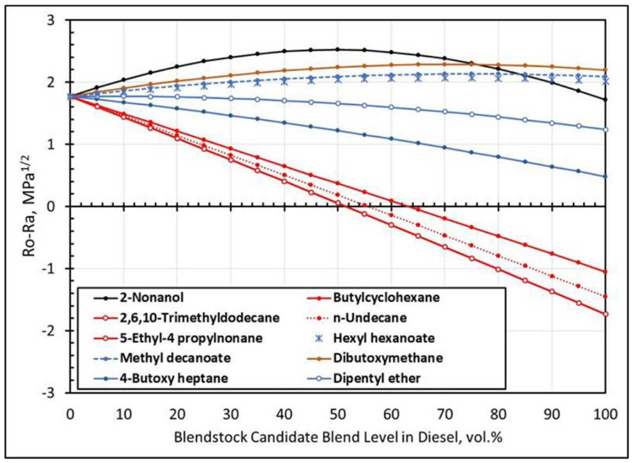

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FIGURE A.4 Solubility curves for NBR (Buna-N) for each of the MCCI fuel candidates as a function of blend level in diesel.

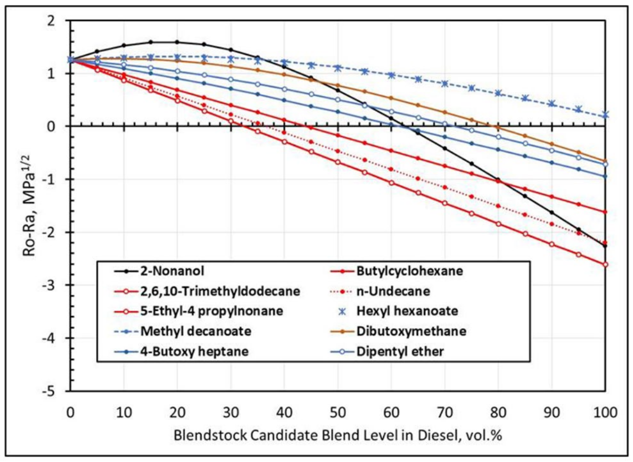

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FIGURE A.5 Solubility curves for neoprene for each of the MCCI fuel candidates as a function of blend level in diesel.

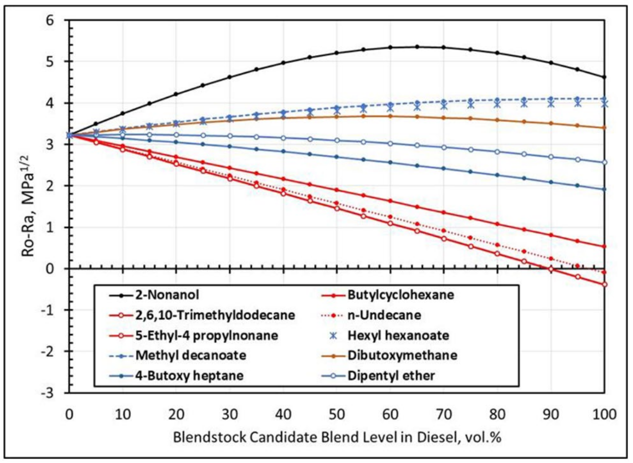

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FIGURE A.6 Solubility curves for epichlorohydrin rubber for each of the MCCI fuel candidates as a function of blend level in diesel.

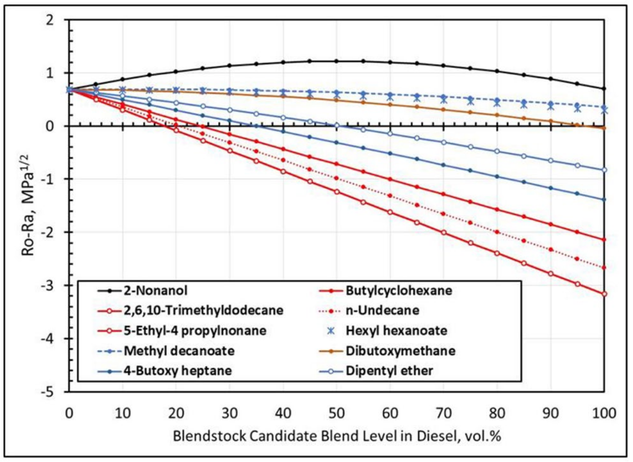

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FIGURE A.7 Solubility curves for PTFE for each of the MCCI fuel candidates as a function of blend level in diesel.

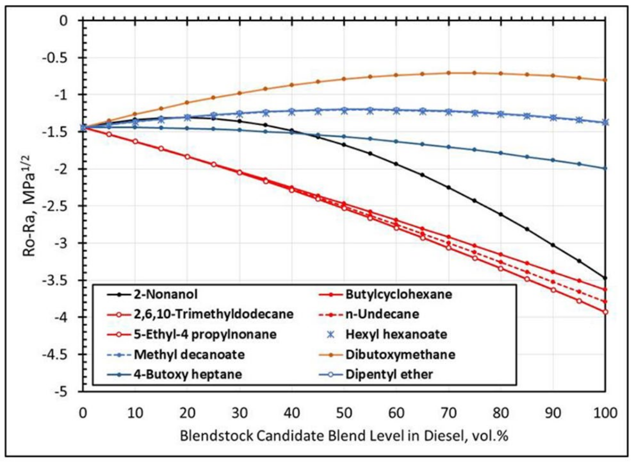

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FIGURE A.8 Solubility curves for PVDF for each of the MCCI fuel candidates as a function of blend level in diesel.

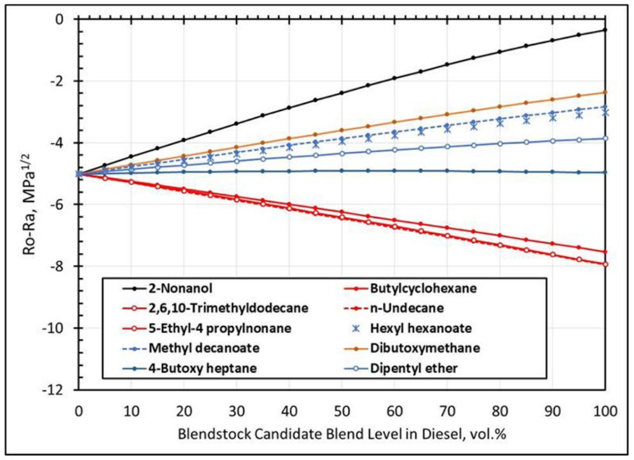

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FIGURE A.9 Solubility curves for POM for each of the MCCI fuel candidates as a function of blend level in diesel.

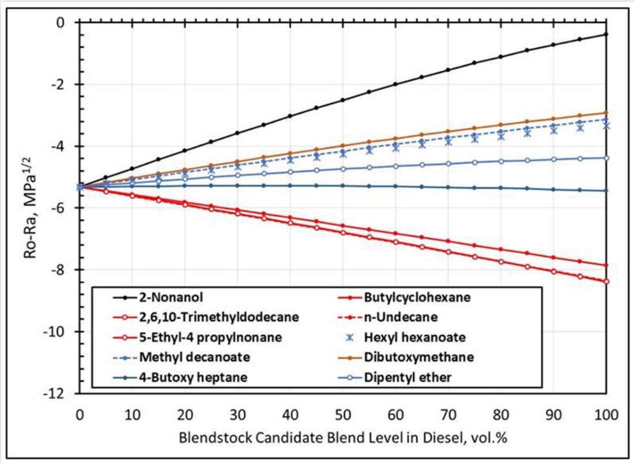

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FIGURE A.10 Solubility curves for Nylon 66 for each of the MCCI fuel candidates as a function of blend level in diesel.

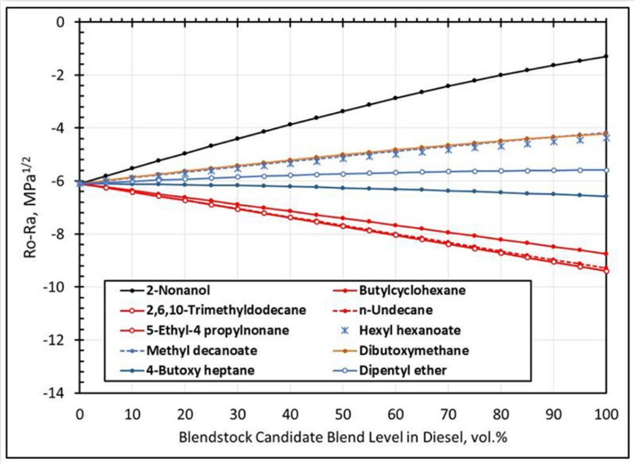

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FIGURE A.11 Solubility curves for Nylon 12 for each of the MCCI fuel candidates as a function of blend level in diesel.

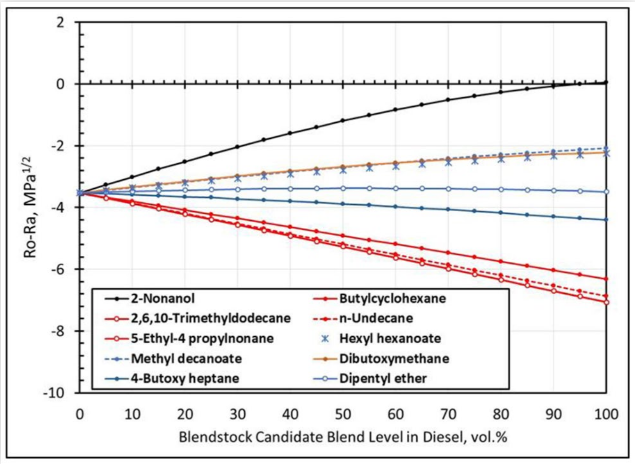

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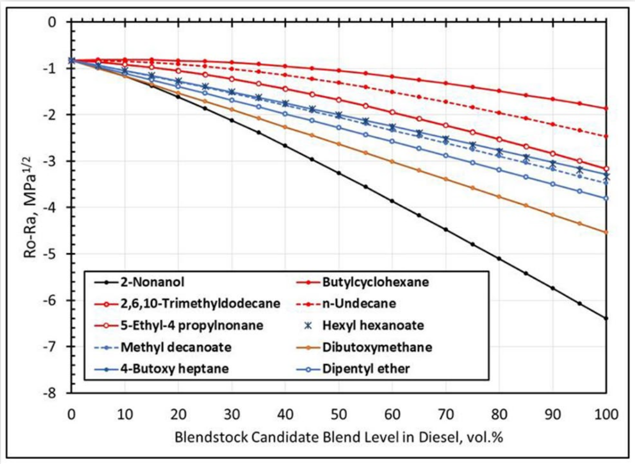
FIGURE A.12 Solubility curves for HDPE for each of the MCCI fuel candidates as a function of blend level in diesel.



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