



Properties of Oxygenates Found in Upgraded Biomass Pyrolysis Oil as Components of Spark and Compression Ignition Engine Fuels

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S Supporting Information

ABSTRACT: Oxygenates present in partially hydroprocessed lignocellulosic-biomass pyrolysis oils were examined for their impact on the performance properties of gasoline and diesel. These included: methyltetrahydrofuran, 2,5-dimethylfuran (DMF), 2-hexanone, 4-methylanisole, phenol, *p*-cresol, 2,4-xyleneol, guaiacol, 4-methylguaiacol, 4-methylacetophenone, 4-propylphenol, and 4-propylguaiacol. Literature values indicate that acute toxicity for these compounds falls within the range of the components in petroleum-derived fuels. On the basis of the available data, 4-methylanisole and by extension other methyl aryl ethers appear to be the best drop-in fuel components for gasoline because they significantly increase research octane number and slightly reduce vapor pressure without significant negative fuel property effects. A significant finding is that DMF can produce high levels of gum under oxidizing conditions. If the poor stability results observed for DMF could be addressed with a stabilizer additive or removal of impurities, it could also be considered a strong drop-in fuel candidate. The low solubility of phenol and *p*-cresol (and by extension, the two other cresol isomers) in hydrocarbons and the observation that phenol is also highly extractable into water suggest that these molecules cannot likely be present above trace levels in drop-in fuels. The diesel boiling range oxygenates all have low cetane numbers, which presents challenges for blending into diesel fuel. There were some beneficial properties observed for the phenolic oxygenates in diesel, including increasing conductivity, lubricity, and oxidation stability of the diesel fuel. Oxygenates other than phenol and cresol, including other phenolic compounds, showed no negative impacts at the low blend levels examined here and could likely be present in an upgraded bio-oil gasoline or diesel blendstock at low levels to make a drop-in fuel. On the basis of solubility parameter theory, 4-methylanisole and DMF showed less interaction with elastomers than ethanol, while phenolic compounds showed somewhat greater interaction. This effect is not large, especially at low blend levels, and is also less significant as the size and number of alkyl substituents on the phenol ring increase.

■ INTRODUCTION

A U.S. Department of Energy study indicates that by 2030 the United States will be capable of producing more than 1.3 billion tons annually of sustainable and primarily lignocellulosic forest and agricultural waste and perennial crops that can be processed into biofuels.¹ A similar National Academy of Sciences study projects that 0.55 billion tons of lignocellulosic-biomass could be sustainably harvested in 2020, which could be used to produce 30 to 45 billion gallons of spark-ignition and diesel engine fuel.² Fast pyrolysis is an attractive process option for biomass conversion because of its relatively low cost³ and greenhouse gas emission reductions relative to petroleum fuels of 51% to 95%, depending on the source of hydrogen used for upgrading and other process options.⁴ The raw product bio-oil contains on the order of 40 wt % oxygen on a dry basis, leading to the requirement for upgrading by hydrodeoxygenation.^{5–7} Allowing some oxygen to remain in the upgraded products may have economic advantages.^{5,8} Here, we report an investigation into the potential for oxygenated compounds present in upgraded lignocellulosic-biomass pyrolysis oils to be components of drop-in gasoline and diesel fuel. Some of the compounds considered here could be produced via other biomass conversion processes as well.

Fast Pyrolysis. Fast pyrolysis, rapid heating to decomposition in the absence of oxygen, is an efficient means of depolymerizing lignocellulosic-biomass.⁹ The process produces a liquid product representing as much as 80% of the starting dry weight of the biomass¹⁰ and about 75% of the energy content.¹¹ Other products of the pyrolysis process include gases, primarily carbon monoxide, carbon dioxide, and methane, as well as solid char and ash. The pyrolysis liquids have been investigated as a potential source of refinery feedstock¹² or as a stand-alone fuel to be used in specially designed boilers to offset petroleum usage. Fast pyrolysis reactors require residence times of only 0.5 to 2 s at temperatures of 400–600 °C.³ Because of the short residence times required, processing can occur in relatively small reactors with fairly low capital costs. Raw pyrolysis oil is a mixture of water (15–30 wt %) and organic oxygen (25–45 wt %) in a wide variety of organic compounds, including carbohydrates, phenols, alcohols, acids, esters, furans, aldehydes, and ketones, as well as some hydrocarbons.^{6,10} The composition depends upon the starting material and the process conditions.¹³ Unoxxygenated

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hydrocarbons make up less than 20% of pyrolysis oil composition.⁵

There are numerous problems with the utilization of raw pyrolysis oil. First, the high water content lowers the net heating value and can increase corrosion. The remaining organic fraction is highly corrosive (even without the presence of water) due to its organic acid content.^{14,15} Many of the components are poorly soluble in petroleum or petroleum products and will readily absorb water.¹⁰ Distillation residue can be as high as 50%.^{16,17} Other problems can include high viscosity,^{18,19} poor stability in storage,²⁰ and the presence of suspended solids.²¹

Pyrolysis oils can be upgraded by hydroprocessing to remove oxygen to a level such that the remaining components are suitable for use in fuel blending or coprocessing with petroleum in a refinery.^{5–7} Processing in a refinery would serve to separate the components on the basis of boiling point into diesel, gasoline, and other products. Various methods for treating the raw pyrolysis oil have been proposed, but the most commonly cited approach is hydroprocessing, in which oil is fed to a high-temperature catalytic reactor for oxygen removal in the presence of added hydrogen. However, costs increase significantly at higher oxygen removal rates (Arbogast, Figure 1).⁸ Complete

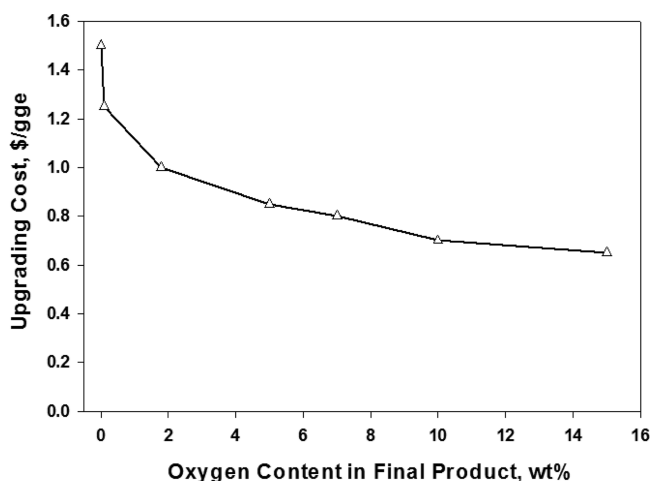


Figure 1. Cost in dollars per gasoline gallon equivalent (gge) for upgrading biomass pyrolysis oil by hydrotreating as a function of product oxygen content (calculated from data presented in ref 8).

removal of oxygen from biomass-pyrolysis oil has not been reported, and studies suggest the cost to do so would be prohibitive. However, rather than treating to complete removal or to concentrations as low as 0.5 wt % oxygen, relatively mild hydrotreating to a somewhat higher residual oxygenate concentration (on the order of 7 wt % oxygen) has been proposed as a less expensive alternative.²²

With less extensive hydrotreating, the total oxygen in the oil is reduced and the relative composition of oxygenates also shifts. As shown in a previous study, compounds with greater oxygen functional group reactivity will be disproportionately reduced.²³ At 8.2 wt % oxygen level, there were significant levels of carboxylic acids, carbonyls, phenols, and ethers. Lowering the oxygen content further to 4.9% eliminated the carbonyl and carboxyl compounds and converted the aryl ethers to phenols, and significant further treatment was required to remove phenolic compounds. In this work, we selected oxygenates representative of those observed in partially hydrotreated pyrolysis oils²³ and measured their properties and performance

in neat form as well as when blended with conventional diesel and gasoline. Our objective was to understand at what level and in what form oxygen might be acceptable in drop-in fuels.

Oxygenate Selection. Christensen and co-workers have analyzed the oxygenated compounds present in the various distillate fractions of hydrotreated pyrolysis oil.²³ From that work, the highest concentration components or classes of components were selected and specific compounds were identified to represent the compound class. These are shown in Figure 2, and the relevant pure component properties are

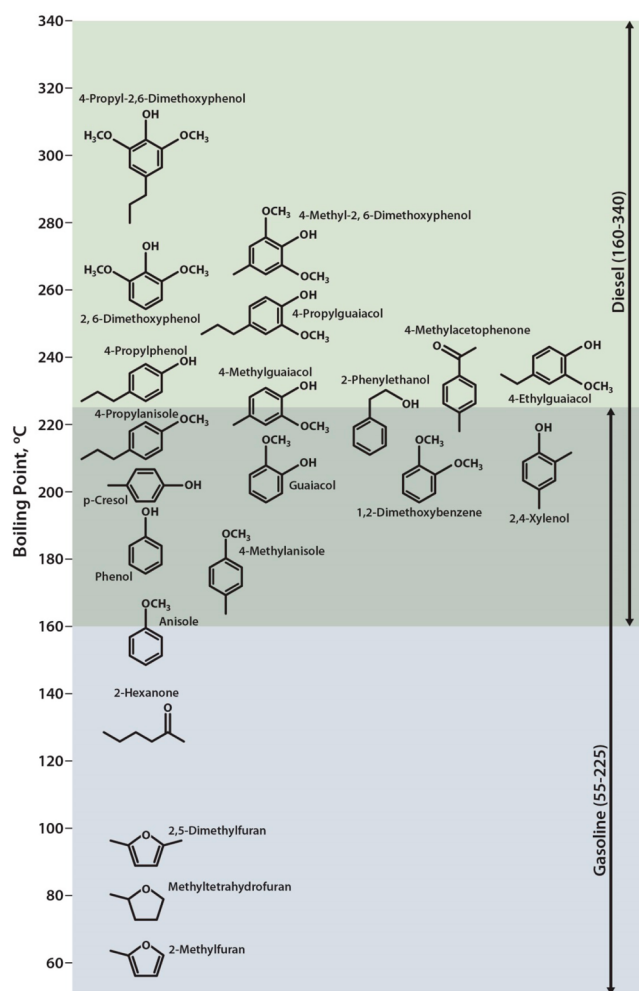


Figure 2. Oxygenate compounds representative of those found in upgraded biomass pyrolysis oils.

listed in Table 1. The concentrations of these components will vary based on the biomass source and processing conditions. A subset of these compounds was evaluated at nominally 2 volume percent (vol %) concentration in the appropriate petroleum product (gasoline or diesel). Assuming a total oxygen concentration for hydrotreated pyrolysis oil of 7 wt % and below, individual oxygenates may be present at concentrations lower than 2 vol %. However, in this case, we are investigating the oxygenate as being representative of a specific compound class and thus selected the higher concentration. Additionally, several oxygenates were evaluated at slightly higher concentration (nominally 6 vol %), and because 2,5-dimethylfuran (DMF)²⁴ and 4-methylanisole (4-MA)²⁵ (representing a mixture of methyl aryl ethers) have been proposed as stand-alone blending oxygenates, they were tested at roughly 10 vol % or higher.

Table 1. Relevant Fuel Properties of Pure Oxygenates Identified in Hydroprocessed Pyrolysis Oils^a

class/compound	boiling point (°C)	blending RON and MON ^b	cetane number (or DCN ^c)	net heating value (MJ/L)	flash point (°C)	density at 25 °C (g/mL)	melting point (°C)	solubility in water at 20 °C (wt %)	oral LD ₅₀ (rat) (mg/kg)
2-methylfuran	64 ²⁶	155, 92 ²⁷	8.9 ²⁸	27.60 ²⁷	−17 ²⁹	0.910 ³⁰	−89 ²⁹	0.3 ³⁰	480 ²⁹
methyltetrahydrofuran	79²⁶	85, 76²⁷	22²⁸	28.18²⁷	−11²⁹	0.86²⁹	−136²⁶	12.1³⁰	4,500²⁹
2,5-DMF	94²⁶	153, 109²⁷	10.9²⁸	30.13²⁷	7²⁹	0.903²⁹	−62²⁹	0.26³⁰	1,238²⁹
2-hexanone	127²⁶	--	--	28.35^e	23²⁹	0.812²⁹	−57²⁶	2³¹	2,590²⁹
anisole	154 ²⁶	119, 98 ³²	6 ^d	33.19 ^e	52 ²⁹	0.995 ²⁹	−23 ²⁶	insoluble ²⁹	3,700 ²⁹
4-MA	177²⁶	166, 148³³	7^d	33.38^d	59²⁹	0.969²⁹	−32²⁶	insoluble²⁹	1,920²⁹
phenol	182²⁶	--	--	33.34^e	79²⁹	1.071²⁹	41²⁶	8.8³⁴	317²⁹
p-cresol	202²⁶	153, 149³⁵	--	33.73^e	85²⁹	1.034²⁹	34²⁶	2.1³⁶	207²⁹
guaiacol	205²⁶	--	19^d	31.06^d	82²⁹	1.129²⁹	28²⁶	1.7³⁷	520²⁹
1,2-dimethoxybenzene	206 ²⁶	--	17 ^d	29.7 ^d	72 ²⁹	1.084 ²⁹	15 ²⁶	insoluble ³¹	890 ²⁹
2,4-xyleneol	211²⁶	140, 113³⁵	--	34.21^e	94²⁹	1.011²⁹	25²⁶	0.79³⁶	3,200²⁹
4-propylanisole	215 ²⁶	--	7 ^d	34.22 ^d	90 ²⁹	0.941 ²⁹	−5 ^b	slight ³⁸	4,400 ²⁹
2-phenylethanol	218 ²⁶	111 ^f	8 ^d	34.78 ^d	102 ²⁹	1.02 ²⁹	−19 ²⁶	2 ³¹	1,790 ²⁹
4-methylguaiacol	221²⁶	--	20^d	31.57^d	99²⁹	1.092²⁹	5²⁹	slight³⁸	740²⁹
4-methylacetophenone	226²⁶	--	--	34.15^d	82²⁹	1.005²⁹	−64²⁶	0.04⁴⁰	1,400²⁹
4-propylphenol	232²⁶	--	9^d	34.16^d	106²⁹	0.983²⁹	22²⁶	insoluble³¹	348²⁹
4-ethylguaiacol	235 ²⁹	--	20 ^d	30.48 ^d	108 ²⁹	1.063 ²⁹	15 ²⁹	slight ³⁸	— ^g
4-propylguaiacol	250²⁹	--	18^d	32.66^d	113²⁹	1.038²⁹	16²⁶	slight³⁸	2,600²⁹
2,6-dimethoxyphenol	263 ²⁶	--	26 ^d	28.63 ^d	140 ²⁹	1.134 ³⁹	55 ²⁹	2 ⁴¹	550 ²⁹
4-methyl-2,6-dimethoxyphenol	268 ⁴⁰	--	25 ^d	29.09 ^d	113 ²⁹	1.105 ⁴⁰	40 ²⁹	insoluble ²⁹	1,700 ⁴¹
4-propyl-2,6-dimethoxyphenol	299 ⁴¹	--	--	--	135 ⁴¹	1.074 ⁴¹	--	insoluble ⁴¹	--

^aCompounds in bold text are included in gasoline/diesel blending. --: Indicates value unknown. ^bRON = research octane number; MON = motor octane number. ^cDCN = derived cetane number as measured by ASTM D6890. ^dMeasured in this study. ^eCalculated from density and higher heating value in ref 26. ^fBlending RON measured for 15 vol % blend in 93.4 RON toluene standard fuel, this work. ^gUsed as food and fragrance additive.

In addition to fuel performance properties, oxygenate toxicity is also of concern. While recognizing the limitations of this approach, rat oral median lethal dose (LD₅₀) values can be used to provide a preliminary comparison of the toxicity of the biomass oxygenates with toxicity of components of gasoline. The U.S. Environmental Protection Agency uses four categories to rank acute toxicity of pesticide products:⁴²

- Category I – Highly toxic and severely irritating (LD₅₀ ≤ 50 mg/kg).
- Category II – Moderately toxic and moderately irritating (LD₅₀ 51–500 mg/kg).
- Category III – Slightly toxic and slightly irritating (LD₅₀ 501–5,000 mg/kg).
- Category IV – Practically nontoxic and not an irritant (LD₅₀ > 5,000 mg/kg).

LD₅₀ values for selected gasoline components are listed in Table 2 (these components are commonly included as hazardous components in material safety data sheets for gasoline and diesel fuel). None of the components of gasoline or the biomass oxygenates are in Category I, but there are compounds in Category II in both groups. Additionally, benzene, cumene, and naphthalene are listed in the U.S. Department of Health and Human Services 13th Report on Carcinogens.⁴³ None of the biomass oxygenates are so listed. It therefore seems reasonable to draw a preliminary conclusion that the biomass oxygenates do not present additional toxicity challenges relative to conventional gasoline and diesel fuels.

METHODS

Materials. The base spark-ignition fuel (referred to as Base E0 Gasoline) was a summer suboctane blendstock for oxygenate blending

Table 2. Toxicity of Some Common Fuel Components⁴⁴

compound	rat oral LD ₅₀ (mg/kg)
toluene	636
n-hexane	25,000
xylene (all isomers)	4,300
isooctane	>5,000
ethanol	7,060
1,2,4-trimethylbenzene	5,000
n-pentane	400
cumene ^a	1,400
ethylbenzene	3,500
benzene ^a	930
cyclohexane	12,705
naphthalene ^a	490
1-methylnaphthalene	1,840

^aBenzene is listed as a known human carcinogen. Cumene and naphthalene are listed as substances reasonably anticipated as being human carcinogens.⁴³

(BOB) previously described in Christensen and co-workers.²⁷ The model pyrolysis oxygenates were blended with the ethanol-free BOB and E10 made from that BOB (referred to as Base E10 Gasoline). E10 was included because nearly all of the gasoline consumed in the United States today contains 10 vol % ethanol, and a potential future scenario is blending of other biomass-derived streams into E10. The diesel was a certification diesel obtained from Haltermann Solutions. Properties of the hydrocarbon base fuels are included in the Supporting Information (Tables SI-1 and SI-2). Oxygenate blend components were purchased from commercial suppliers and used without further purification. Purities of purchased compounds were verified by gas chromatography (GC) with flame ionization detection (Table SI-3, Supporting Information). Most were better than 99 wt % purity. Blending was

Table 3. Volatility Properties of Blends of Pyrolysis Oil Components with E0 Gasoline and E10 Gasoline

	vapor pressure (psi)	distillation T_{10} (°C)	distillation T_{50} (°C)	distillation T_{90} (°C)	distillation final BP (°C)	$T_{V/L=20}$ (°C)
	ASTM D5191	ASTM D86	ASTM D86	ASTM D86	ASTM D86	ASTM D5188
ASTM D4814 standard ^a	<7.8	<70	77 to 121	<190	<225	>54
base E0 gasoline	5.31	68	106	173	222	76.6
base E10 gasoline	6.47	60	101	171	217	--
10% 4-MA	5.04	70	114	177	218	>80
13% 2,5-DMF	5.16	72	101	169	220	78
2% methyl-tetrahydrofuran	--	67	104	171	219	--
2% 2-hexanone	--	68	106	173	221	--
6% 2-hexanone	--	66	106	175	220	--
1% phenol	--	66	106	175	220	--
2% <i>p</i> -cresol	--	64	106	174	215	--
2% 2,4-xyleneol	--	68	108	180	219	--
2% guaiacol	--	66	107	175	216	--
2% 4-methylguaiacol	--	67	108	179	219	--

^aThe BOB used here is intended for blending of a Class AA E10, and the required values for this class are listed here.

performed gravimetrically, and the values were converted to volume percent for reporting of results as this is more commonly used in the fuel industry. Concentrations of each oxygenate blended into gasoline and diesel were confirmed by GC. Details of the GC method are reported in the Supporting Information.

Test Methods. ASTM methods were performed without modification. Gasoline and diesel blends were evaluated using the test methods required in ASTM D4814-14 and D975-14, respectively. Additionally, a number of other properties such as net heating value, water content, density, and acid number were determined using ASTM methods. Peroxide content was determined using American Oil Chemists' Society method CD 8b-90, modified for potentiometric titration. Potential for water extraction by exposure to an aqueous layer was examined as in Christensen et al.²⁷ Briefly, each blended fuel was exposed to 10 vol % water and shaken to saturate the hydrocarbon layer. The mixture was left to separate overnight. The water content of the hydrocarbon layer was determined by Karl Fischer titration (ASTM D6304), and the amount of oxygenate extracted into the water layer was determined by GC.

In addition to measuring gasoline blend stability by ASTM D525 (as required by ASTM D4814), gasoline stability was also assessed using the ASTM D873 standard test method for oxidation stability of aviation fuels. This method is used to assess the potential for fuels to form gum and deposits under accelerated aging conditions. This method is similar to D525 in that the fuel is thermally stressed in a vessel pressurized with oxygen; however, with D873, the amounts of gums and insolubles formed as a result of oxidation are measured rather than the amount of time the fuel takes to reduce the pressure of the vessel through reaction with oxygen as in D525. D873 is conducted at 100 °C under 700 kPa of oxygen for 16 h. Diesel fuel blends were assessed for oxidation stability using the ASTM D4625 long-term storage method and the Rapid Small Scale Oxidation Test (RSSOT) method ASTM D7545, as well as for thermal stability using ASTM D6468 conducted for 180 min at 150 °C.

Compatibility with Elastomers. The concept of solubility parameters was used to characterize compatibility with elastomers for most of the compounds tested in blends. The solubility parameter approach is widely used to predict chemical compatibility. Pioneered by Hildebrand in the form of a single solubility parameter,⁴⁵ it has been expanded by Hansen to include three different parameters⁴⁶ (Hansen solubility parameters).

The use of solubility parameters is based on the concept that similar compounds will have an affinity for each other and 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 a high affinity. Literature values of solubility parameters for specific elastomers were developed on the basis of chemical compatibility with a range of liquids.⁴⁷ A solubility parameter "distance" value R_a is calculated as a

mathematical function of the difference between the three parameters for the two compounds of interest. This is compared to the radius of solubility sphere R_o , which was determined for each elastomer based on previous experimentation and a somewhat arbitrary assessment of what is an acceptable level of interaction between the elastomer and the liquid.⁴⁷ A lower value for R_a/R_o indicates greater affinity between the fluid and the elastomer. An R_a/R_o of less than one suggests that the liquid has a high affinity for the elastomer and a significant potential for negative interaction. An R_a/R_o greater than one suggests that the elastomer will be relatively unaffected by the liquid. Where experimental data are not available, as was the case for solubility parameters for most of the oxygenates, Hansen solubility parameters were developed on the basis of a chemical group contribution method.⁴⁸ In these calculations, gasoline was modeled as a surrogate blend of seven components (Table SI-4, Supporting Information).

RESULTS

Properties of Neat Oxygenates. Representative oxygenates are listed in Table 1, which is a compilation of key fuel property data from literature sources and in-house measurements. Looking at compounds in the gasoline boiling point range (i.e., with boiling points below the T_{90} of gasoline: 185 or 190 °C), both furans and anisoles show high octane number, relatively high net heating value and density combined with low melting point and low solubility in water, suggesting that compounds of these types could function as drop-in gasoline blendstocks. 2-Hexanone also appears to be compatible with gasoline; however, its octane number is unknown, and there may be potential for gum formation by condensation reactions. Methyltetrahydrofuran and phenol have significant water solubility, suggesting their use as drop-in fuel components would be challenging. In addition, phenol has a high melting point. Cresol, guaiacol, xyleneol, 4-propylanisole, 2-phenylethanol, and 4-methylguaiacol all boil above the T_{90} but below the end point (225 °C) of gasoline. This significantly limits the level at which these can be blended, regardless of other properties. Nevertheless, they have high octane number and energy density along with low water solubility but also have a high melting point. These compounds could be considered as components of both gasoline and diesel fuel. The higher boiling compounds (>225 °C) could be considered as drop-in diesel components based on physical properties; however, they have low cetane numbers.

On the basis of these considerations, the oxygenates in the rows with bold text of Table 1 were further examined as potential

residual oxygenates that might be acceptable at low levels after blending with a conventional diesel or gasoline. Certain oxygenates such as DMF, 2-methylfuran, anisole, and 4-MA have desirable gasoline blending properties and could be utilized as a high octane blendstock, either as a neat blending component similar to the way ethanol is used today or as a mixture of similar compounds (furans or methyl aryl ethers). DMF and 4-MA were examined at higher blend levels to simulate use as a neat blend component or as representative of a blendstock consisting of several similar components.

Properties of Gasoline–Oxygenate Blends. Volatility properties are critical for ensuring proper vehicle operation at specific ambient conditions. The Base E0 Gasoline used here is a summertime blendstock, and results for blend volatility properties are shown in Table 3. DMF and 4-MA were blended at 13 vol % and 10 vol %, respectively, while other oxygenates were blended at lower levels. Both DMF and 4-MA slightly lowered vapor pressure, in contrast to the increase observed for ethanol. 4-MA increased T_{50} by 8 °C, but other distillation parameters were only slightly affected by the two higher blend level oxygenates. These changes are considered desirable from the standpoint of petroleum refiners in that they allow blending of additional high-volatility and low-cost petroleum components such as butane while still meeting existing limits on vapor pressure and T_{50} . The oxygenates tested at lower levels had little or no impact on distillation parameters. Blending of the oxygenates had little impact on gasoline density or viscosity (Table SI-5, Supporting Information). There was also little effect on volumetric net heating value (MJ/L) (Table SI-5, Supporting Information), a parameter important to consumers who purchase fuel on a volume basis. 4-MA had no measurable effect on heating value at the 10% blend level, as expected given that its pure component heating value is slightly higher than that of the gasoline blendstock. Blending of DMF caused a small decrease (1.2%) in net heating value.

As shown in Table 4, both 4-MA and DMF significantly increased research octane number (RON) and motor octane number (MON) when blended with the Base E0 Gasoline. Octane number is a critical gasoline performance property as engines are designed to operate without engine knock on

Table 4. Octane Number of Blends of Pyrolysis Oil Components with E0 Gasoline and E10 Gasoline

	RON	MON
	ASTM D2699	ASTM D2700
base E0 gasoline	85.8	81.2
base E10 gasoline	91.6	--
10% 4-MA	90.7	83.1
13% 2,5-DMF	95.0	84.8
2% methyltetrahydrofuran	86.0	--
2% 2-hexanone	86.1	--
6% 2-hexanone	86.1	--
1% phenol	86.7	--
2% <i>p</i> -cresol	88.3	--
6% <i>p</i> -cresol	91.9	--
2% 2,4-xyleneol	89.0	--
2% guaiacol	86.2	--
2% 4-methylguaiacol	86.4	--
2% 2-hexanone/E10	91.4	--
2% <i>p</i> -cresol/E10	93.2	--
2% guaiacol/E10	91.8	--

gasoline meeting the minimum requirement. The volumetric blending RON and MON of 4-MA were 134.8 and 100.2, significantly lower than the values reported by Singerman,^{25,33} although this should not be surprising given the large errors associated with estimation of blending octane numbers from a single concentration level. Blending RON and MON for DMF was 156.6 and 108.9, similar to volumetric blending values reported by Christensen et al.²⁷ We also estimated blending RON for 2-hexanone (90.8) and *p*-cresol (187.5) using the 6 vol % blend level data.

None of the blends showed any evidence of copper or silver strip corrosion (Table SI-6, Supporting Information), properties important for ensuring compatibility with vehicle fuel system materials. Gasoline must be adequately stable to avoid gum formation over a reasonable length of time in the vehicle fuel tank. Two measurements of gasoline stability were employed. ASTM D525, a pass/fail test of stability under oxidizing conditions, showed only that, at the concentrations measured, all of the oxygenate blends passed (Table SI-6, Supporting Information). The results of ASTM D873, which provides a quantitative measure of the tendency for fuels to form gums under accelerated thermal and oxidative aging conditions, showed significant effects for some oxygenates (Table 5). In

Table 5. Gum Formation on D873 Test for Blends of Pyrolysis Oil Components with E0 Gasoline and E10 Gasoline

	gum formation (mg/100 mL)
	ASTM D873
base E0 gasoline	20.2
base E10 gasoline	22.4
10% 4-MA	22.7
13% 2,5-DMF	713
2% methyltetrahydrofuran	1.4
2% 2-hexanone	14.2
6% 2-hexanone	64.1
1% phenol	12.1
2% <i>p</i> -cresol	9.9
6% <i>p</i> -cresol	33.4
2% 2,4-xyleneol	4.5
2% guaiacol	4
2% 4-methylguaiacol	9.7
2% 2-hexanone/E10	34.7
2% <i>p</i> -cresol/E10	23.5
2% guaiacol/E10	22

this test, the fuel is held at 100 °C under 700 kPa of oxygen for 16 h and the mass of insoluble material (gum) formed is determined. Blending of 2-hexanone at the 6 vol % level caused a small increase in gum formation. Most notably, the 13% DMF blend produced a large amount of insoluble gum, over 700 mg/100 mL of fuel. This experiment was replicated with similar results. A blend of 10% DMF in reagent grade isooctane was also tested and produced almost as much gum, 573 mg/100 mL. Figure 3 shows a photo of the aged DMF isooctane blend. The gum is likely formed by an oxidation reaction because a 20 vol % DMF-gasoline blend can fail the ASTM D525 stability test. D525 uses the same apparatus and conditions as D873, but the pressure is measured over time in order to determine oxidation induction time. Fuels with induction time exceeding 240 min meet the ASTM D4814 specification requirements. We are currently investigating this reaction in more detail, as well as the potential of antioxidant additives to control or eliminate it.

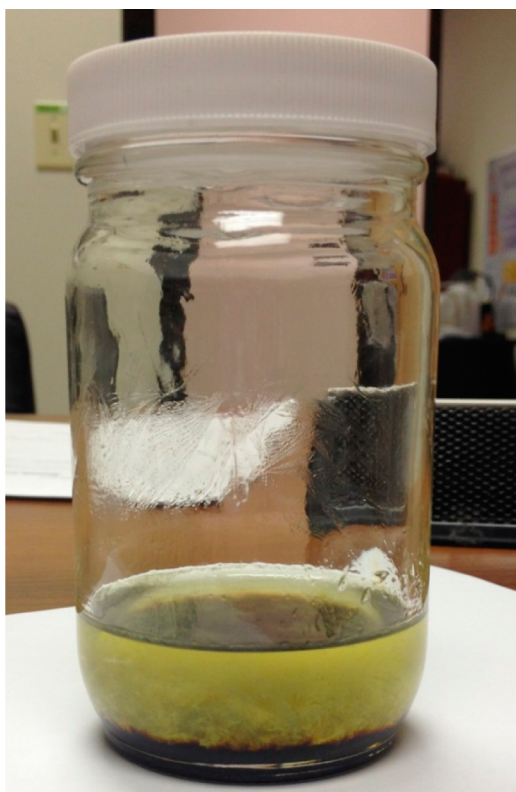


Figure 3. 10% DMF in isooctane blend after aging on the D873 test. Photo from Melissa Legg, Southwest Research Institute, NREL 32488.

Separation of the gasoline into two liquid phases or into a liquid and a solid phase at cold temperatures can lead to vehicle operational issues including failure of the engine to start. Phase separation temperature results are shown in Figure 4. Both phenol and *p*-cresol (and by extension, the two other cresol isomers) significantly increase phase separation temperature at low blending levels, indicating limited solubility in gasoline hydrocarbons. The presence of 10% ethanol eliminated this effect, indicating that ethanol increases their solubility. The other components had no measurable adverse effect on phase separation temperature. Fuels, including gasoline, are sometimes exposed to water during transport and storage. Absorption of high amounts of water into the fuel or extraction of fuel components into a tank water bottom layer can cause fuel properties to change such that performance requirements are no longer met. Not surprisingly, polar oxygenates increase the amount of water absorbed by gasoline, most markedly with *p*-cresol (Table 6). Almost 30% of the phenol dissolved in gasoline will be extracted in the presence of water. For an E10 blend, this experimental procedure causes phase separation to form hydrocarbon–ethanol and ethanol–water phases. While phase separation of ethanol–gasoline blends is extremely rare, should this occur a significant fraction of the biomass oxygenate would also separate into the ethanol–water phase, as shown in Table 6. Given the water extractability and uptake properties of phenol and cresols, it seems unlikely that these molecules could be present at above trace levels in drop-in fuels. A possible route toward utilizing phenol and cresol in gasoline, and improving the fuel properties of other phenolics, is reaction with methanol to produce methyl aryl ethers such as anisole and 4-MA from phenol and *p*-cresol, respectively. These reactions have been

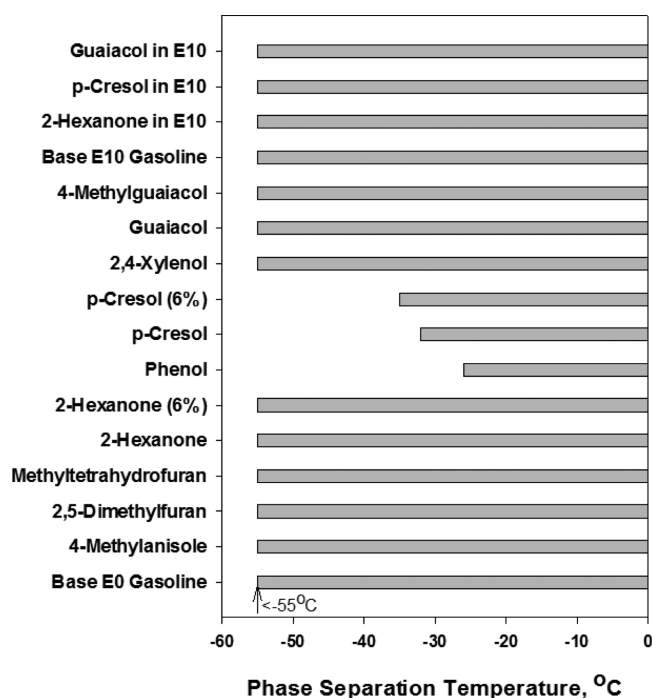


Figure 4. Effect of biomass oxygenates on gasoline phase separation temperature by ASTM method D6422 (−55 °C was the lowest test temperature).

Table 6. Water Absorption and Oxygenate Extraction for Blends of Pyrolysis Oil Components with E0 Gasoline and E10 Gasoline

	water absorbed at saturation (ppm)	oxygenate % extracted by water
	ASTM D6304	NREL GC method
base E0 gasoline	137	NA
base E10 gasoline	654	61.8
10% 4-MA	271	0
13% 2,5-DMF	183	0
2% methyltetrahydrofuran	217	1.1
2% 2-hexanone	245	0
6% 2-hexanone	361	0.7
1% phenol	275	29.8
2% <i>p</i> -cresol	578	4.4
6% <i>p</i> -cresol	1906	3.7
2% 2,4-xylenol	344	0.7
2% guaiacol	256	2.5
2% 4-methylguaiacol	161	0.5
2% 2-hexanone/E10	634	4.2
2% <i>p</i> -cresol/E10	1817	20.8
2% guaiacol/E10	832	19.1

performed with high yield over industrially robust catalysts such as γ -alumina⁴⁹ and ZSM5 zeolite.⁵⁰

Properties of Diesel–Oxygenate Blends. A minimum cetane number is necessary for diesel fuels to ensure that fuel ignition occurs at the appropriate time, allowing the engine to provide its design fuel economy and emissions performance. Because of the relatively low cetane number of all of the diesel boiling range (>160 °C) biomass oxygenates, they were tested at relatively low blend levels. Consequently, many properties show little or no impact from oxygenate blending. These include net heating value and density at 15 °C (important from the

standpoint of volumetric fuel economy), viscosity at 40 °C (which must fall within a specified range for proper functioning of the fuel pump), distillation T_{90} , and carbon residue (which are controlled to avoid injector tip and combustion chamber carbon deposits), as reported in Table SI-7, Supporting Information. Fuels must not be corrosive to fuel system materials. The oxygenates had no effect on acid value or copper corrosion (Table SI-8, Supporting Information).

Controlling cloud point is critical for ensuring the engine can operate without fuel filter clogging in cold weather. Perhaps surprisingly, as reported in Table SI-8, Supporting Information, only very small impacts on cloud point were observed in spite of the high melting point of most of the oxygenates used for blending. A minimum electrical conductivity is required to prevent the buildup of static charge and the potential for a spark discharge to ignite the fuel. Many of the oxygenates increased conductivity, as shown in Figure 5. However, the conductivity of

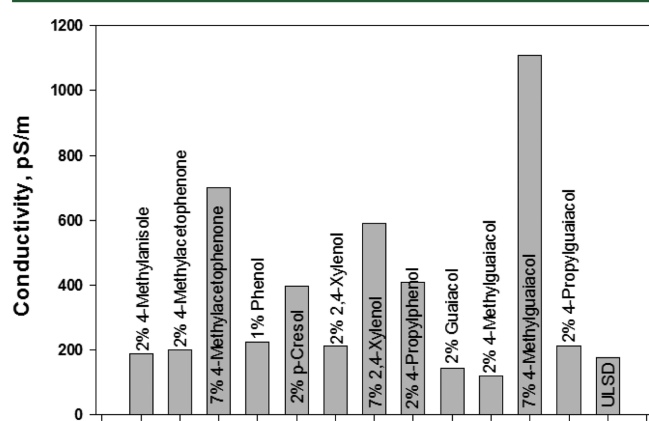


Figure 5. Conductivity in pico-Siemens/meter (pS/m) measured for diesel-oxygenate blends (25 pS/m minimum required by ASTM D975).

the base ultralow sulfur diesel was well above the minimum requirement (25 pS/m in ASTM D975), and the largest conductivity changes required relatively high oxygenate blend levels. Nevertheless, the results suggest that these biomass oxygenates will not negatively impact electrical conductivity.

As noted, a minimum cetane number is required to achieve the desired combustion timing. In some cases, the change in cetane number for oxygenate blending was significant, as shown in Table 7. In particular, significant reductions were observed at the nominally 6 vol % blend level for 2,4-xylenol and 4-methylguaiacol. Fuel pumps in diesel engines are lubricated by the fuel, which must have a minimum level of lubricity to avoid excessive fuel pump wear. The phenolic compounds all caused an improvement in fuel lubricity (that is, a reduction in wear scar diameter), as shown in Figure 6. Notably, the base diesel fuel was out of specification and exceeded the maximum wear scar diameter requirement in ASTM D975. Phenol, 4-methylguaiacol, and 4-propylguaiacol were the most effective for lubricity improvement.

Fuels must be stable and not form gums during oxidation in storage and under high temperature conditions encountered in the engine fuel system. Long-term storage stability was assessed using the ASTM D4625 12-week test for blends of diesel with 4-MA and 2,4-xylenol 2 vol % blends. No increase in acids or insolubles was detected, while peroxide content increased moderately from about 6 to 24 ppm. Stability was also assessed using the RSSOT method. This test measures an induction time

Table 7. Derived Cetane Number for Diesel-Oxygenate Blends

DCN	
	ASTM D6890
Cert diesel	43
B5 (w/Cert diesel)	44
2% 4-MA	41.5
2% 4-methylacetophenone	41.6
7% 4-methylacetophenone	40.6
1% phenol	41.6
2% <i>p</i> -cresol	40.3
2% 2,4-xylenol	40.2
7% 2,4-xylenol	35.5
2% 4-propylphenol	41.5
2% guaiacol	41.6
2% 4-methylguaiacol	41.2
6% 4-methylguaiacol	38.3
2% 4-propylguaiacol	42.7
2% 4-methylacetophenone/B5	43
2% 2,4-xylenol/B5	41.1
2% 4-methylguaiacol/B5	42

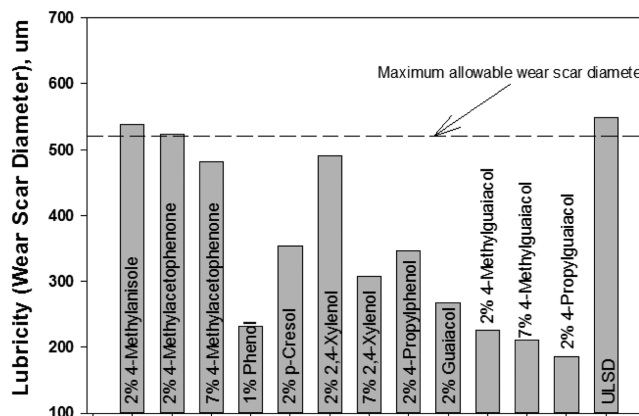


Figure 6. Lubricity (wear scar diameter by ASTM D6079) for the diesel-oxygenate blends (520 μm maximum limit in ASTM D975).

for the onset of oxidation. Results are shown in Figure 7. Clearly, the phenolic oxygenates are acting as antioxidants in diesel fuel by causing an increase in induction time. The oxygenates had no

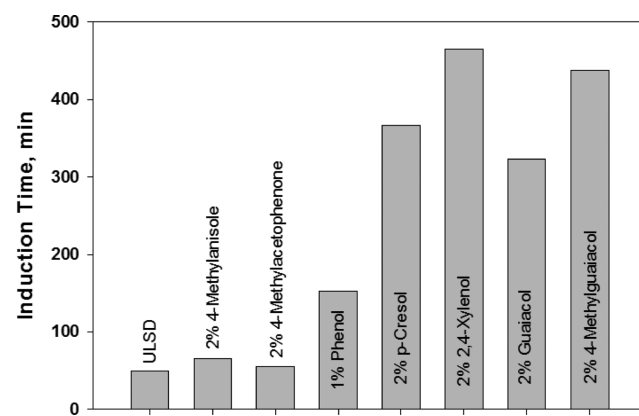


Figure 7. Diesel fuel oxidation stability for the biomass-oxygenate blends as measured by the ASTM D7545 (RSSOT) method.

effect on thermal stability as measured by ASTM D6468 (Table SI-8, Supporting Information).

Elastomer Compatibility. Three elastomers commonly used in vehicle fuel systems were considered: silicone, fluoroelastomer, and hydrogenated nitrile butadiene rubber (HNBR). The solubility parameter simulation considered most of the biomass oxygenates blended into a surrogate gasoline (a mixture of seven pure components). Diesel fuel which has 25% aromatic content has similar Hansen solubility parameters to those of gasoline (not shown), and a similar analysis would show comparable trends to those for gasoline. The Parker O-Ring Handbook⁵¹ supports this with virtually identical compatibility ratings for gasoline and diesel with the 18 elastomers considered, with the exception of one elastomer type (polyacrylate).

As noted in the Methods section, the lower the value of R_a/R_o , the greater the affinity. An R_a/R_o of less than one suggests that the liquid has a high affinity for the elastomer and thus a significant potential for negative interaction. An R_a/R_o greater than one suggests that the elastomer will be relatively unaffected by the liquid. Figure 8 shows that the gasoline surrogate is fully compatible with the fluoroelastomer having $R_a/R_o > 1$, while HNBR is reasonably compatible with a ratio of about 0.87. The silicone elastomer is not particularly compatible with gasoline given its low R_a/R_o value. Addition of oxygenates to the gasoline has little impact on the fluoroelastomer. The oxygenates do

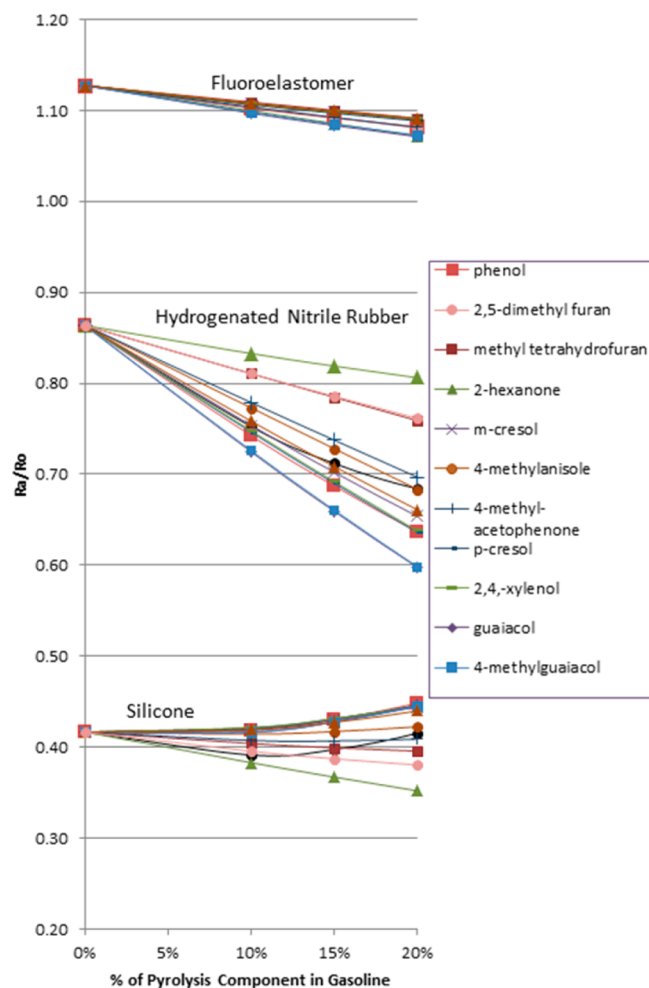


Figure 8. Relative compatibilities of pyrolysis fuel components in gasoline. Higher R_a/R_o means more compatibility.

impact the compatibility of HNBR. Both DMF and 4-MA have less of an effect than ethanol. The phenolic compounds have greater impact than ethanol, although this difference is small for 4-propylphenol and also small at blend levels below 5 vol %.

CONCLUSIONS

On the basis of the available data, 4-MA and by extension other methyl aryl ethers appear to be the best drop-in fuel components for gasoline because they significantly increase RON and slightly reduce vapor pressure without significant negative fuel property effects. If the poor stability results observed for DMF could be addressed with a stabilizer additive or removal of impurities, it could also be considered a strong drop-in fuel candidate. The low solubility of phenol and *p*-cresol (and by extension, the two other cresol isomers) in hydrocarbons and the observation that phenol is also highly extractable into water suggest that these molecules cannot likely be present above trace levels in drop-in fuels. Other oxygenates, including other phenolic compounds, showed no negative impacts at the low blend levels examined here and could likely be present in an upgraded bio-oil gasoline stream at low levels and blended with conventional gasoline to make a drop-in fuel.

The diesel boiling range oxygenates all have low cetane numbers, which presents challenges for blending into diesel fuel. For blending at more than residual levels, the benefits of renewable carbon at a high energy density have to be adequate to justify the use of cetane improver additives or a higher cetane number petroleum blendstock. However, it is important to note that this study only examined oxygenates that might be present in hydroprocessed biomass pyrolysis oils. These oils will be predominantly hydrocarbons, and this study has not examined the fuel performance properties of these hydrocarbons. Other than low cetane numbers, the biomass oxygenates did not exhibit negative impacts on the properties measured. Note, however, that while extraction into water was not measured for diesel, phenol could be expected to exhibit the same high extractability from diesel fuel as was shown for gasoline. For the same reasons that phenol, and probably also cresols, are unsuitable as drop-in gasoline blend components, they are also unlikely to be suitable in diesel. There were some beneficial properties observed for the phenolic oxygenates, including increasing conductivity, lubricity, and oxidation stability of the diesel fuel.

On the basis of solubility parameter theory, 4-MA and DMF showed less interaction with elastomers than ethanol did, while phenolic compounds showed somewhat greater interaction. This effect is not large, especially at low blend levels, and is also less significant as the size and number of alkyl substituents on the phenol benzene ring increases.

ASSOCIATED CONTENT

Supporting Information

Tables of base fuel properties, gasoline–oxygenate blend properties, and diesel–oxygenate blend properties. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Perlack, R. D.; Wright, L. L.; Turhollow, A. F.; Graham, R. L.; Stokes, B. J.; Erbach, D. C. *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply*; DOE/GO-102995-2135; Oak Ridge National Laboratory: Oak Ridge, TN, April 2005.
- (2) *Liquid Transportation Fuels from Coal and Biomass: Technological Status, Costs, and Environmental Impacts*; National Academy of Sciences-National Academy of Engineering-National Research Council Report; The National Academies Press: Washington, DC, 2009; ISBN-10:0309-137128.
- (3) Mohan, D.; Pittman, C. U.; Steele, P. H. *Energy Fuels* **2006**, *20*, 848–889.
- (4) Han, J.; Elgowainy, A.; Palou-Rivera, I.; Dunn, J. B.; Wang, M. Q. *Well-to-Wheels Analysis of Fast Pyrolysis Pathways with GREET*; Argonne National Laboratory: Argonne, IL, November 2011, ANL/ESD/11-8.
- (5) Talmadge, M. S.; Baldwin, R. M.; Biddy, M. J.; McCormick, R. L.; Beckham, G. T.; Ferguson, G. A.; Czernik, S.; Magrini-Bair, K. A.; Foust, T. D.; Metelski, P. D.; Hetrick, C.; Nimlos, M. R. *Green Chem.* **2014**, *16*, 407–453.
- (6) Zacher, A. H.; Loarte, M. V.; Santosa, D. M.; Elliott, D. C.; Jones, S. B. *Green Chem.* **2014**, *16*, 491–515.
- (7) Wang, H.; Male, J.; Wang, Y. *ACS Catal.* **2013**, *3*, 1047–1070.
- (8) Arbogast, S.; Bellman, D.; Paynter, J. D.; Wykowski, J. *Fuel Process. Technol.* **2012**, *104*, 121–127.
- (9) Scott, D. S.; Piskorz, J. *Can. J. Chem. Eng.* **1982**, *60* (5), 666–674.
- (10) Czernik, S.; Bridgewater, A. V. *Energy Fuels* **2004**, *18*, 590–598.
- (11) Carpenter, D.; Westover, T. L.; Czernik, S.; Jablonski, W. *Green Chem.* **2014**, *16*, 384–406.
- (12) Jones, S.; Valkenburg, C.; Walton, C.; Elliott, D.; Holladay, J.; Stevens, D.; Kinchin, C.; Czernik, S. *Production of Gasoline and Diesel From Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case*; Pacific Northwest National Laboratory: Richland, WA, Feb. 2009, PNNL-18284.
- (13) Qu, T.; Guo, W.; Shen, L.; Xiao, J.; Zhao, K. *Ind. Eng. Chem. Res.* **2011**, *50*, 10424–10433.
- (14) Oasmaa, A.; Peacocke, C. *Properties and Fuel Use of Biomass-Derived Fast Pyrolysis Liquids. A Guide*; VTT Publications: Finland, 2010; Vol. 731, 134 p.
- (15) Oasmaa, A.; Sipilä, K. *Pyrolysis Oil Properties: Use of Pyrolysis Oil as Fuel in Medium-Speed Diesel Engines. In Bio-Oil Production and Utilisation: Proceedings of the 2nd EU-Canada Workshop on Thermal Biomass Processing*; Bridgewater, A. V., Hogan, E. N., Eds.; CPL Press: Newbury, U.K., 1996; pp 175–185.
- (16) Marsman, J. H.; Wildschut, J.; Evers, P.; de Koning, S.; Heeres, H. *J. J. Chromatogr. A* **2008**, *1188*, 17–25.
- (17) Oasmaa, A.; Czernik, S. *Energy Fuels* **1999**, *13*, 914–921.
- (18) Diebold, J. P.; Czernik, S. *Energy Fuels* **1997**, *11*, 1081–1091.
- (19) Nolte, M. W.; Liberatore, M. W. *Energy Fuels* **2011**, *25*, 3314–3317.
- (20) Diebold, J. P. *A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils*; NREL Report SR-570-27613; National Renewable Energy Laboratory: Golden, CO, 2000; 59 pp.
- (21) Baldwin, R. M.; Feik, C. J. *Energy Fuels* **2013**, *27*, 3224–3238.
- (22) French, R. J.; Stunkel, J.; Baldwin, R. M. *Energy Fuels* **2011**, *25* (7), 3266–3274.
- (23) Christensen, E.; Chupka, G.; Luecke, J.; Alleman, T. L.; Iisa, K.; McCormick, R. L.; Franz, J. A.; Elliott, D. C. *Energy Fuels* **2011**, *25* (11), 5462–5471.
- (24) Zhong, S.; Daniel, R.; Xu, H.; Zhang, J.; Turner, D.; Wyszynski, M. L.; Richards, P. *Energy Fuels* **2010**, *24*, 2891–2899.
- (25) Singerman, G. M. *Methyl Aryl Ethers from Coal Liquids as Gasoline Extenders and Octane Improvers*; SAE Technical Paper No. 810443; SAE International: Warrendale, PA, USA, 1981.
- (26) NIST Chemistry Webbook; <http://webbook.nist.gov/chemistry/> (accessed December 10, 2014).
- (27) Christensen, E.; Yanowitz, J.; Ratcliff, M.; McCormick, R. L. *Energy Fuels* **2011**, *25* (10), 4723–4733.
- (28) Sudholt, A.; Cai, L.; Heyne, J.; Haas, F. M.; Pitsch, H.; Dryer, F. L. *Proc. Combust. Inst.* **2014**, DOI: 10.1016/j.proci.2014.06.147.
- (29) Material Safety Data Sheet; www.sigmaaldrich.com (accessed November 26, 2014).
- (30) Yanowitz, J.; Christensen, E.; McCormick, R. L. *Utilization of Renewable Oxygenates as Gasoline Blending Components*; Technical Report NREL/TP-5400-50791; National Renewable Energy Laboratory: Golden, CO, August 2011.
- (31) Material Safety Data Sheet; www.chemicalbook.com (accessed November 11, 2014).
- (32) Zhou, L.; Boot, M. D.; Johansson, B. H.; Reijnders, J. J. E. *Fuel* **2014**, *115*, 469–478.
- (33) Singerman, G. *Methyl Aryl Ethers from Coal Liquids as Gasoline Extenders and Octane Improvers*; DOE/CE/50022-1; Contract Number DE-AC01-79CS50022; Office of Transportation Programs: Washington, DC, November 1980.
- (34) Narasimhan, K. S.; Reddy, C. C.; Chari, K. S. *J. Chem. Eng. Data* **1962**, *7* (3), 340–343.
- (35) Buether, H.; Kobylinski, T. P. *ACS Div. Petr. Chem. Prepr.* **1982**, *27* (4), 880–889.
- (36) Donhal, V.; Fenclova, D. *J. Chem. Eng. Data* **1995**, *40*, 478–483.
- (37) Material Safety Data Sheet; www.acros.com (accessed November 11, 2014).
- (38) Food and Agricultural Organization of the United Nations; www.fao.org/ag/agn/jecfa-flav/ (accessed November 10, 2014).
- (39) Material Safety Data Sheet; www.guidechem.com (accessed November 11, 2014).
- (40) Material Safety Data Sheet; www.lookchem.com (accessed November 10, 2014).
- (41) www.thegoodscentscompany.com (accessed November 10, 2014).
- (42) Labeling Requirements for Pesticides and Devices, Code of Federal Regulations, Title 40, Part 156, Subpart D, 156.62; <http://www.ecfr.gov/cgi-bin/ECFR?page=browse> (accessed November 17, 2014).
- (43) 13th Report on Carcinogens; U.S. Department of Health and Human Services, October 2, 2014; <http://ntp.niehs.nih.gov/pubhealth/roc/roc13/index.html#P> (accessed November 22, 2014).
- (44) Toxicology Data Network; National Institutes of Health; <http://toxnet.nlm.nih.gov/> (accessed November 17, 2014).
- (45) Hildebrand, J. H.; Scott, R. L. *The Solubility of Nonelectrolytes*, 3rd ed.; Reinhold Publishing Corp: New York, 1950; 488 pp.
- (46) Hansen, C. M. *J. Paint Technol.* **1967**, *39* (S05), 104–117.
- (47) Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*, 2nd ed.; CRC Press: Boca Raton, FL, 2007; 544 pp.
- (48) Stefanis, E.; Panayiotou, C. *Int. J. Thermophys.* **2008**, *29* (2), 568–585.
- (49) Samolada, M. C.; Grigoriadou, E.; Kiparissides, Z.; Vasalos, I. A. *J. Catal.* **1995**, *152*, 52–62.
- (50) Renaud, M.; Chantal, P. D.; Kaliaguine, S. *Can. J. Chem. Eng.* **1986**, *64*, 787–791.
- (51) *Parker O-Ring Handbook*; ORD 5700; Parker Hannifin Corporation: Cleveland, OH; http://www.parker.com/literature/ORD%205700%20Parker_O-Ring_Handbook.pdf (accessed May 24, 2014).