Impact of Lignocellulosic Biomass-Derived Oxygenates on Diesel Fuel Properties and Engine Emissions

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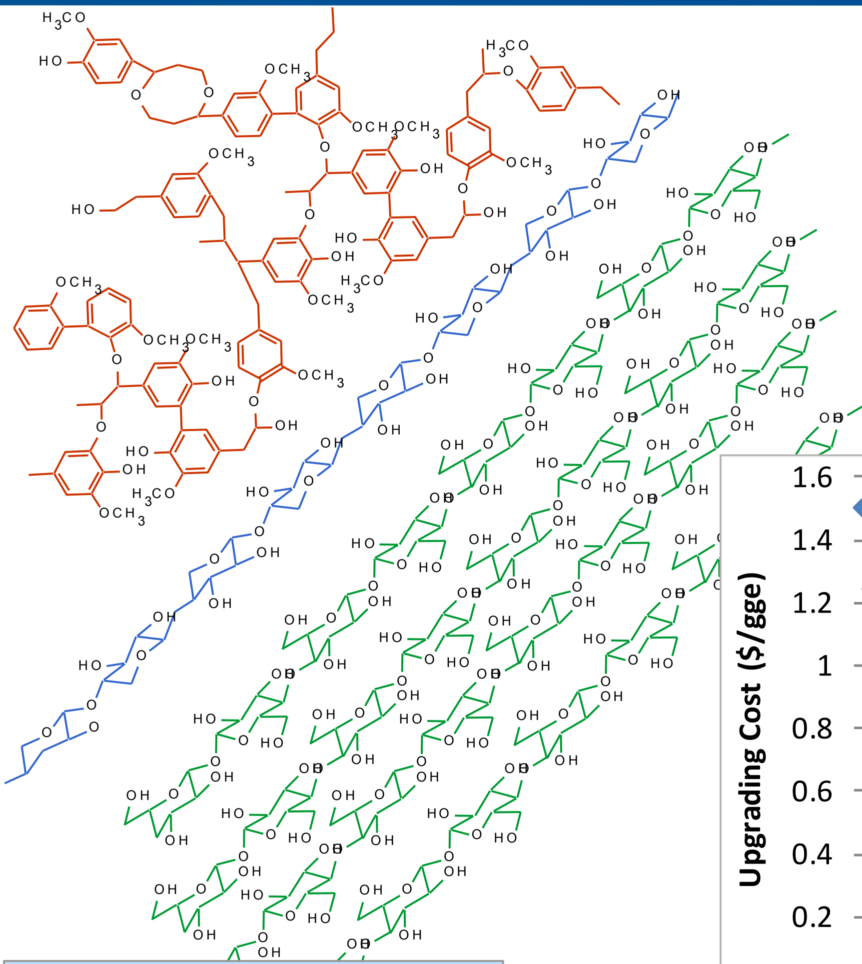
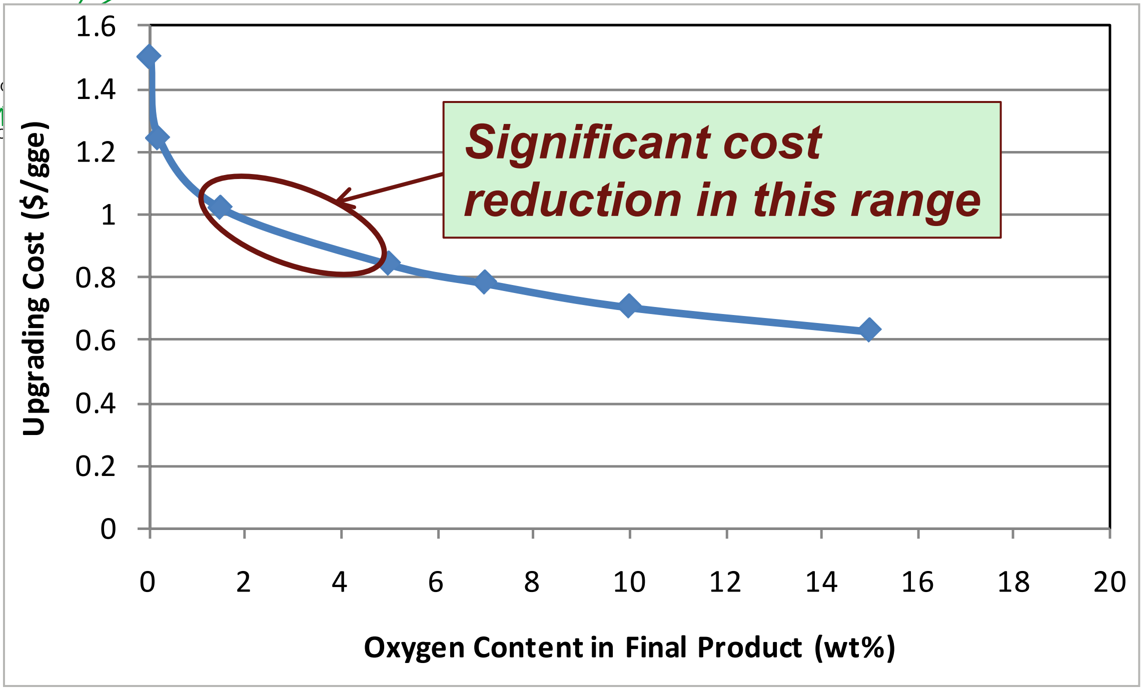
Biomass to Hydrocarbon Biofuels?



Lignin: 15%–25%
Hemicellulose: 23%–32%
Cellulose: 38%–50%

- Biomass has high oxygen content:
  - 40 to 60 wt%
  - Molar O/C about 0.6
- Economically rejecting this oxygen may not be possible
- Example: hydrotreating costs for fast-pyrolysis oils can be very high

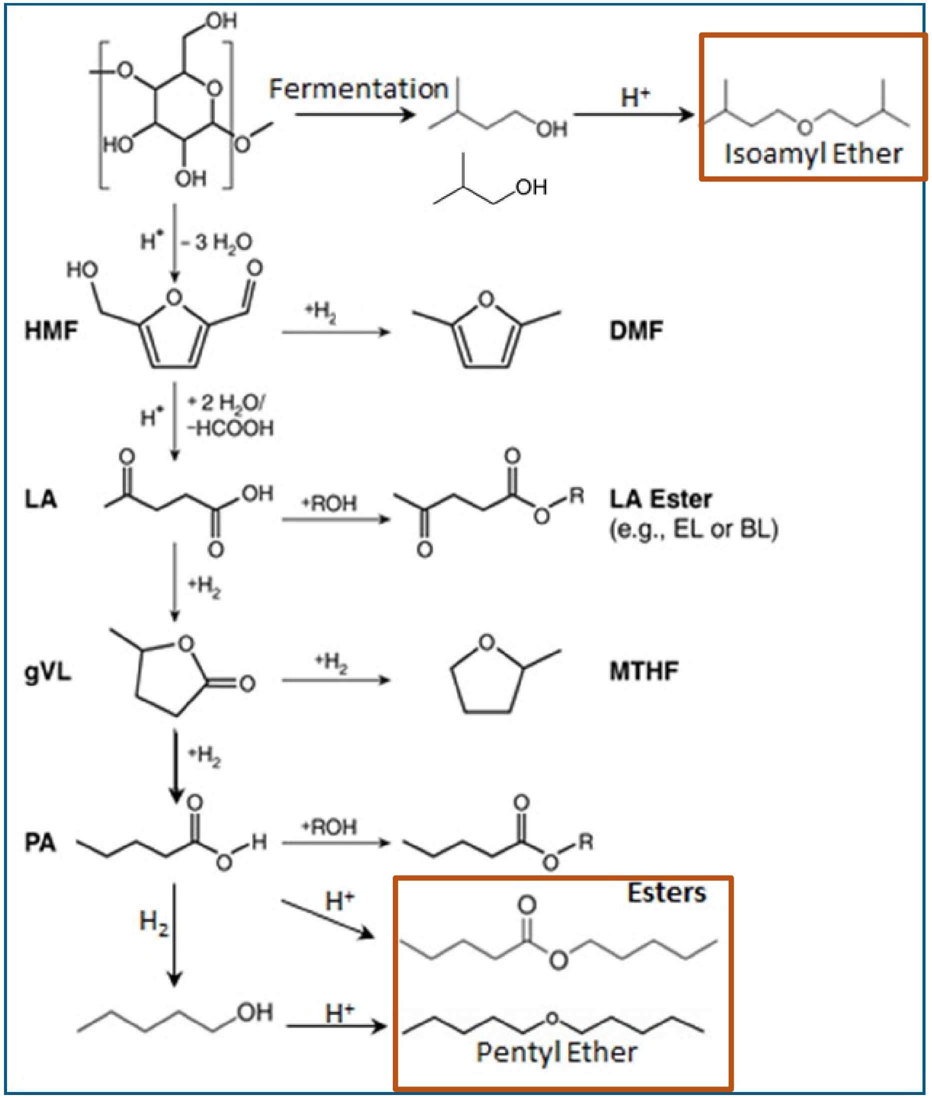


Can Oxygenates Be Tolerated in Drop-in Fuels?

- **Article of faith that "drop-in" fuels are hydrocarbon**
  - Compatible with engines
  - Compatible with fuel distribution (pipeline) and refueling infrastructure
  - Fungible (interchangeable)
- ***Our research seeks to determine if and at what levels biomass-derived oxygenates are scientifically and commercially feasible in drop-in fuels***
- **Can economics be improved if less than 100% of the oxygen is removed?**
- **Properties of biomass-derived oxygenates and diesel blends**
- **CI engine performance and emissions**
- **Gasoline blends/SI engine performance also being studied**

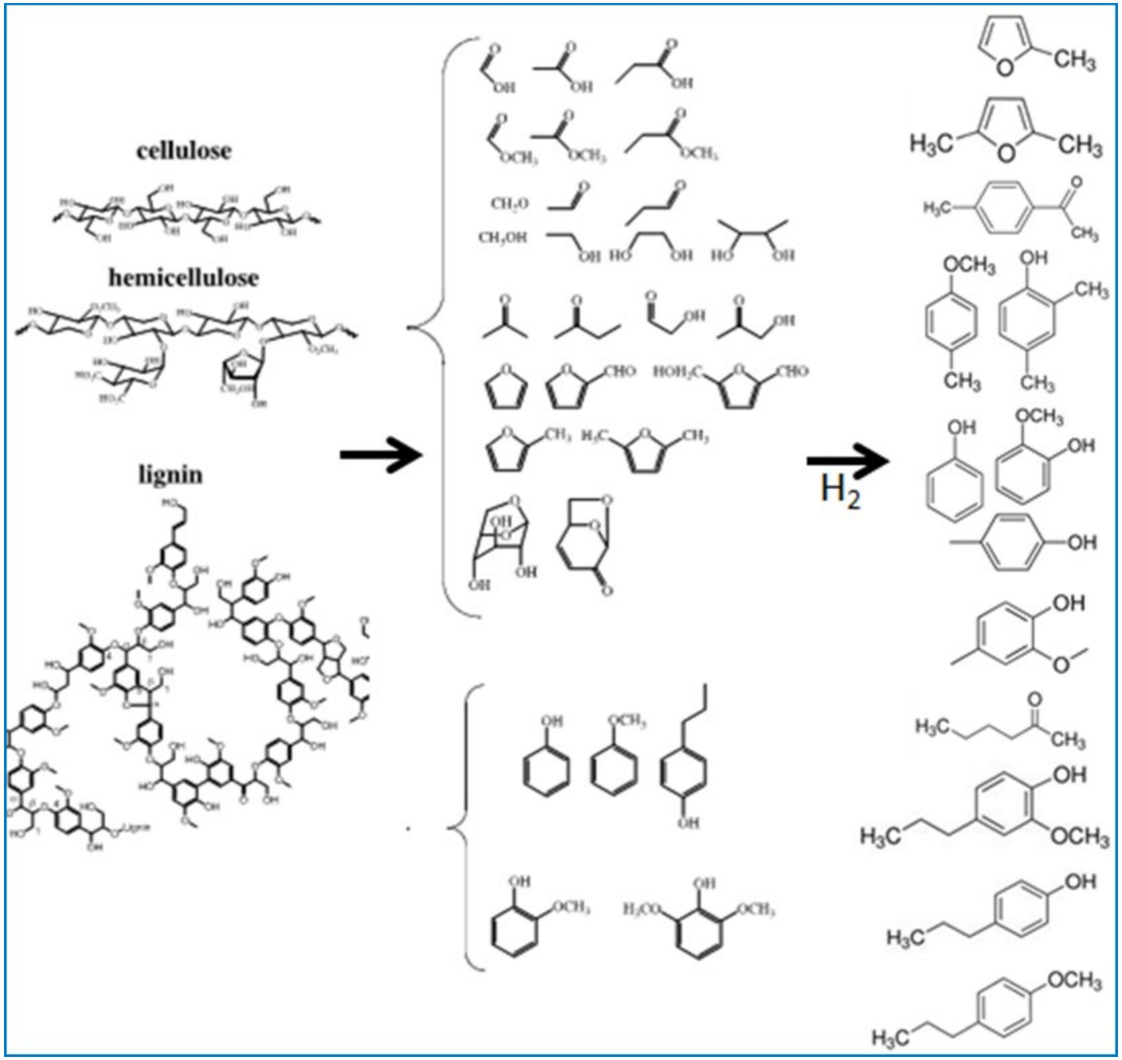
Acid Deconstruction of Biomass

- **Blending components from chemical deconstruction of biomass**
- **Coupling of C5 alcohols and esters to diesel boiling range products**
- **Tested at 10 to 15 wt%**



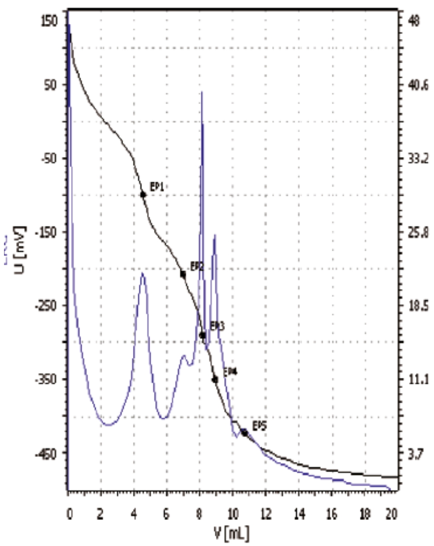
Fast Pyrolysis of Biomass followed by Hydroprocessing

- **Yields primarily oxygenated aromatics**
- **Have not been well characterized in the diesel boiling range**
- **30% to 40% aromatic carbon**
- **Low cetane number (CN) blendstock**
- **Oxygenates potentially tolerable at residual levels (<2% to 3%) in finished fuel?**

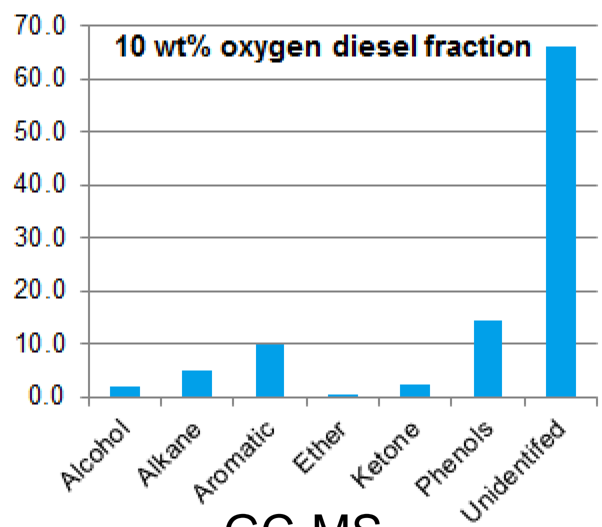


Analytical Results for Hydroprocessed Pyrolysis Oil Boiling Fractions

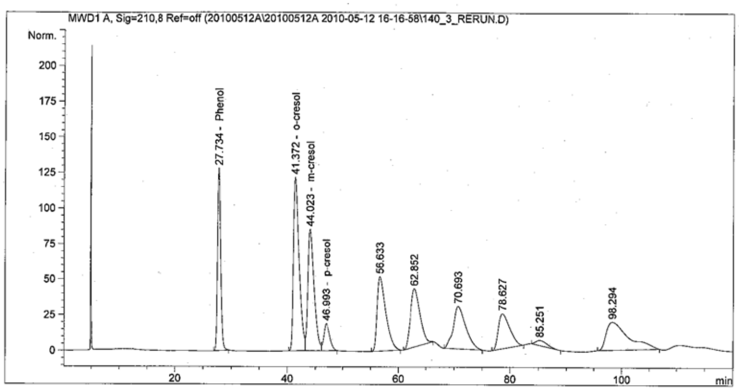
- Bio-oil sample hydroprocessed to three different oxygen levels, then distilled to produce gasoline, jet, and diesel fractions
- Below 5 wt% oxygen, diesel fraction oxygenates are almost entirely phenols, low-level ketones
- Acid titration quantifying multiple endpoints shows no carboxylic acids below 5 wt% oxygen while HPLC shows many unidentified phenolics
- Analysis for carbonyls also shows none below 5 wt% oxygen
- Carbon-13 NMR shows presence of only phenolic oxygen and well over 50% aromatic carbon at any oxygen level of 10% or lower



Acid Titration



GC-MS

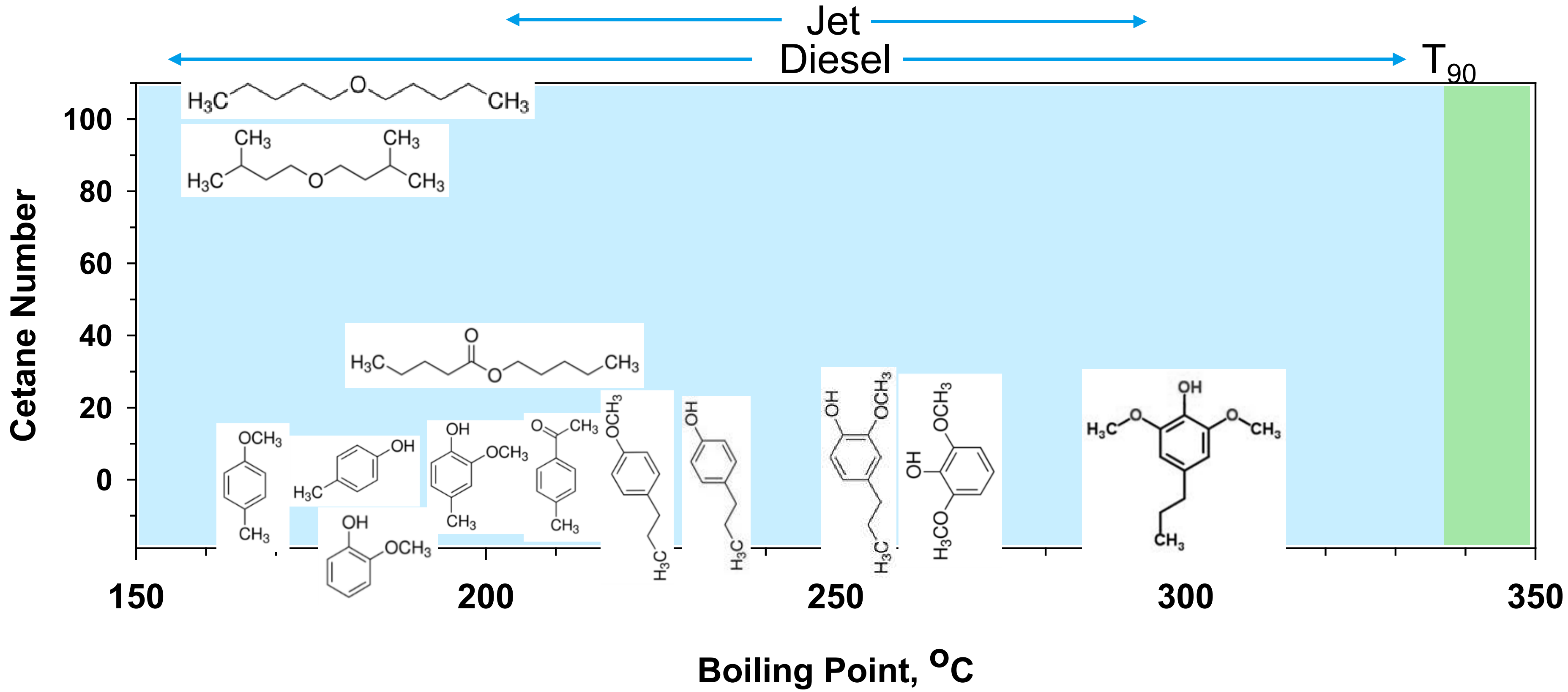


HPLC

Christensen, E., et al., “Analysis of Oxygenated Compounds in Hydrotreated Biomass Fast Pyrolysis Oil Distillate Fractions,” *Energy Fuels* **25** 5462–5471 (2011).

Biomass-Derived Diesel Oxygenate Boiling Points

- High CN pentyl-ethers plus pentyl valerate from acid deconstruction and upgrading chemistry
- Pyrolysis-derived oxygenates are low CN aromatic compounds – identified by GC-MS



Objective and Outline

Objective: Can biomass-derived oxygenates be blended into conventional diesel and still meet the practical requirements of a fungible, drop-in fuel?

1. C5 Esters and Ethers

a. Properties of pure components
b. Properties of blends
c. Combustion and emission results

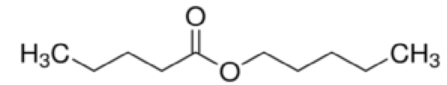
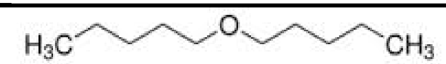
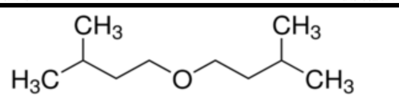
2. Pyrolysis-Derived Oxygenates

a. Properties of pure components
b. Properties of blends
c. Combustion and emission results

3. Elastomer Compatibility

Primary Focus (1a–1b and 2a–2b)

Diesel Boiling Range C5 Esters and Ethers

		Boiling Point, °C	Flashpoint, °C	Freezing Point, °C	Net Heating Value, MJ/L	Density	Water solubility	DCN
Pentylpentanoate		204	81	-79	29.0	0.865	Insoluble	30
Dipentylether		187	57	-69	--	0.785	Insoluble	111
Diisoamylether		173	46	<-80	30.4	0.778	insoluble	96

Physical Properties

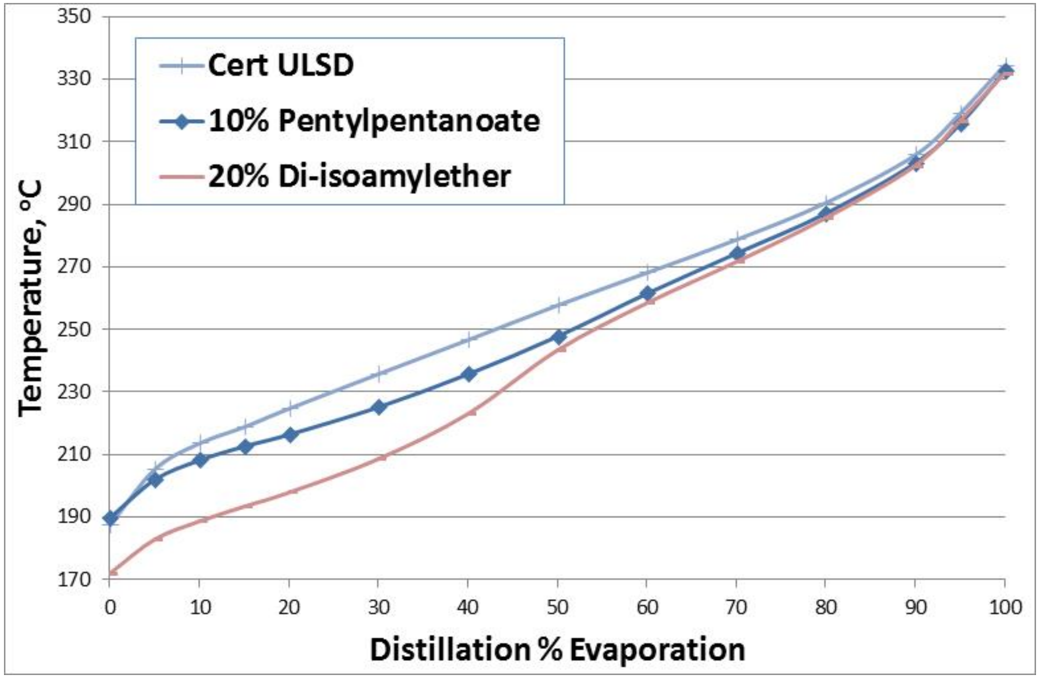
- Boiling in diesel range
- High flashpoint
- Very low melting point
- Reasonable density

Performance Properties

- Heating value 15%–20% lower than diesel
- Very low water solubility
- DCN either very high, or slightly low

Potential poor stability of ethers? No peroxides were observed over 12-week aging of a 20 vol% isoamyl ether blend at 43°C under air.

Properties of Pentyl Pentanoate and Isoamylether Blends

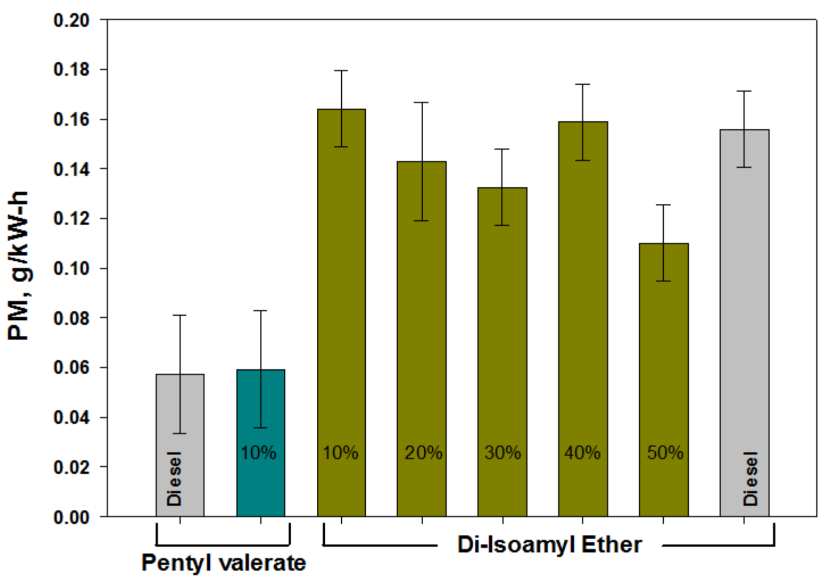


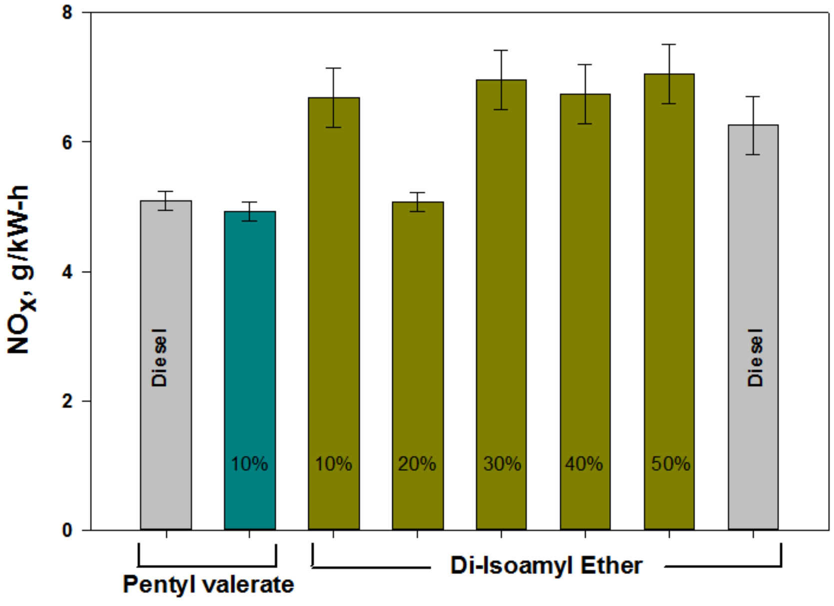
	20% Di-isoamylether	10% Pentyl-pentanoate	Cert ULSD
DCN	47.3	42.2	43.0
Flashpoint, °C	68	77	69
Cloud Point, °C	-33.3	-29.6	-30.1
Conductivity (pS/m)	281	250	178
Oxidation Stability (Total Insoluble mg/100mL)	1.7	0.4	0.5
Thermal Stability (% Reflectance)	99	100	100
Lubricity (Ave. Wear Scar µm)	645	359	548

- **Pentyl pentanoate slightly reduced T10 to T60 bp**
- **Diisoamyl ether significantly reduced T10 through T40 – impact on diesel engine operation unknown**
- **Mostly insignificant changes in fuel properties for blends:**
  - No change in cloud point
  - No change of increase flashpoint
  - Increase DCN by 4 for diisoamylether
  - Oxygenates slightly increased conductivity
  - Changes in oxidation stability (D2274) not regarded as significant
  - No change in thermal stability
  - Pentyl pentanoate significantly improved lubricity
  - Isoamylether negatively impacted lubricity

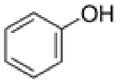
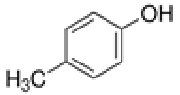
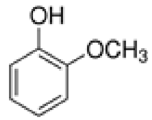
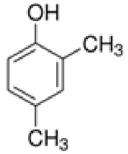
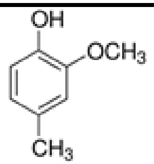
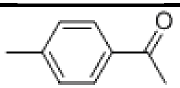
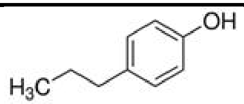
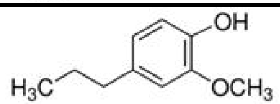
Emission Tests for Pentyl Pentanoate and Isoamylether Blends

- 4-cylinder, turbocharged, 4.5 L John Deere PowerTech Plus common rail, direct injection diesel engine that meets Tier 3/Stage IIIA emissions specifications
- Particulate matter (PM10) was measured gravimetrically
- Changes in emission relative to conventional ULSD are modest
- NO_x emissions reduction for diisoamylether at 20 vol% is significant





Oxygenates Representing Hydroprocessed Biomass Pyrolysis Oil

		Boiling Point, °C	Flashpoint, °C	Freezing Point, °C	Net Heating Value, MJ/L	Density at 25°C	Water solubility, wt%	DCN
4-Methyl anisole		174	59	-32	33.38	0.969	Insoluble	<15
Phenol		181	79	41	34.84	1.071	8.3	<15
p-Cresol		202	85	33	35.47	1.034	1.9	<15
Guaiacol		205	82	27	30.67	1.129	>17	<15
2,4-Xylenol		211	94	23	36.03	1.011	0.5	<15
4-Methyl guaiacol		222	99	5	31.57	1.092	2	<15
4-Methyl acetophenone		226	82	23	34.15	1.005	<1	<15
4-Propyl phenol		232	106	22	34.16	0.983	Insoluble	8.6
4-Propyl guaiacol		250	113		32.66	1.038	<1	18

Hydroprocessed Pyrolysis Oil Oxygenate Properties

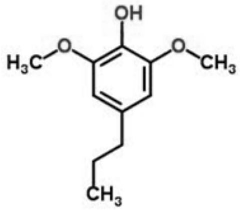
Potentially Positive Attributes

- **Boiling points in diesel range**
- **Flashpoint >52°C**
- **High density**
- **High volumetric heating value**

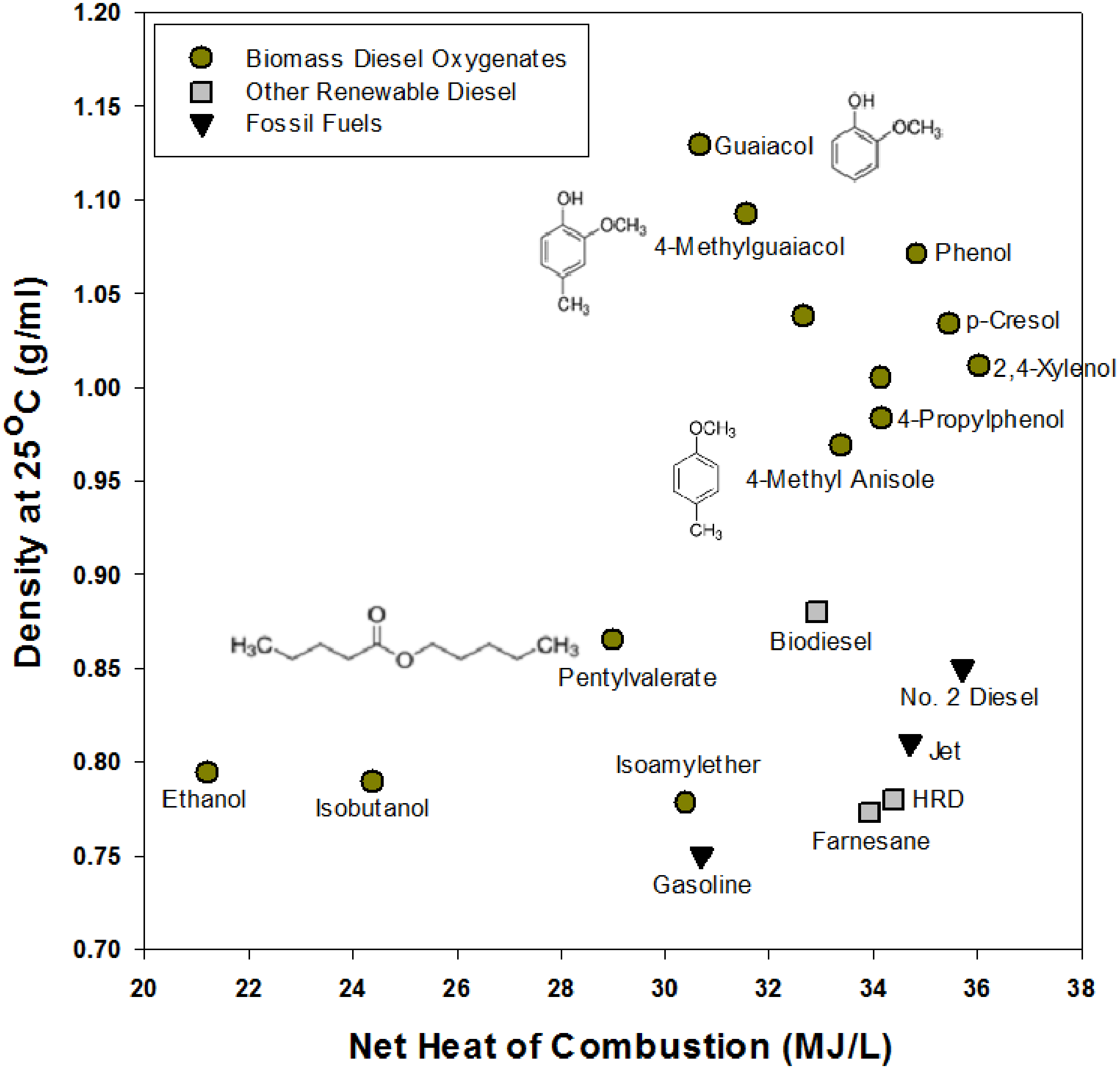
Potentially Negative Attributes

- **High freezing point suggests poor solubility in hydrocarbon**
- **High water solubility of phenol and guaiacol**
- **Low CN**

- **Negative attributes may limit blending to residual levels (<2% oxygenate)**
  - Phenol and guaiacol in particular appear problematic
  - Potential fix to convert phenol to methoxy
- **Is access to renewable carbon at reasonable energy density worth tradeoff in low CN?**
  - Cost of CN improver additive
- **Higher molecular weight oxygenates not yet considered because of difficulty in acquiring pure compound samples**

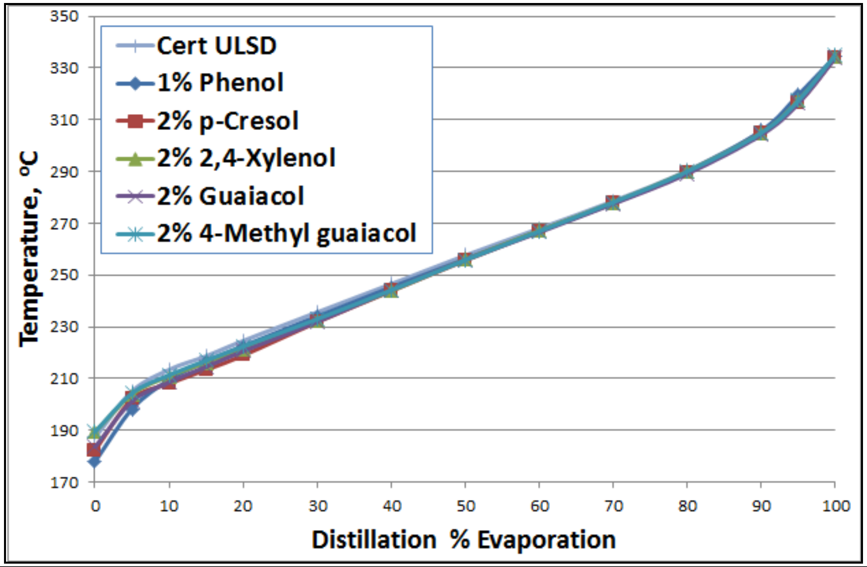


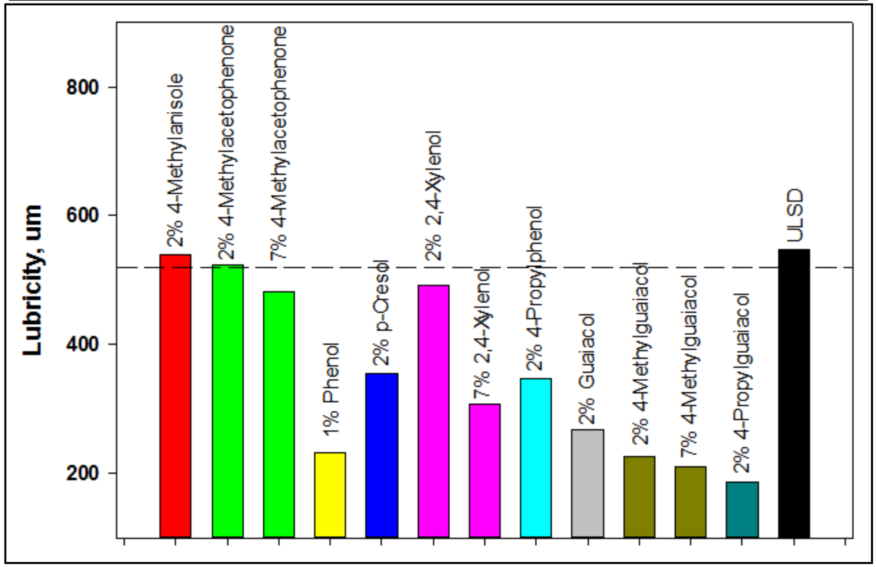
Density and Energy Density of Biomass Oxygenates



Properties of Pyrolysis Oxygenate–Diesel Blends: Residual Levels

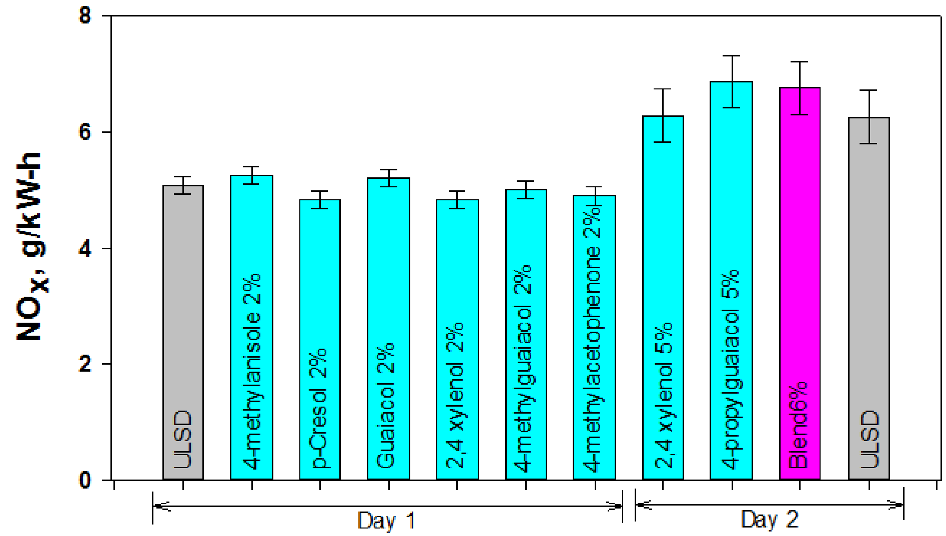
- **No effect on distillation at 2%**
- **No impact on carbon residue, viscosity, copper corrosion or thermal stability**
- **Oxygenates typically increased conductivity and density**
- **No change in cloud point for any oxygenate at 2 to 7 vol% (1 vol% for phenol) (-30°C base fuel)**
- **DCN reduced by 2 to 3 at 2% and 5 or more at 7%**
- **Phenolic compounds improve lubricity**
- **12-week storage stability (D4625) showed no peroxide, acid, or insoluble formation**
  - Phenolics act as antioxidants – significant stability increase on D7545

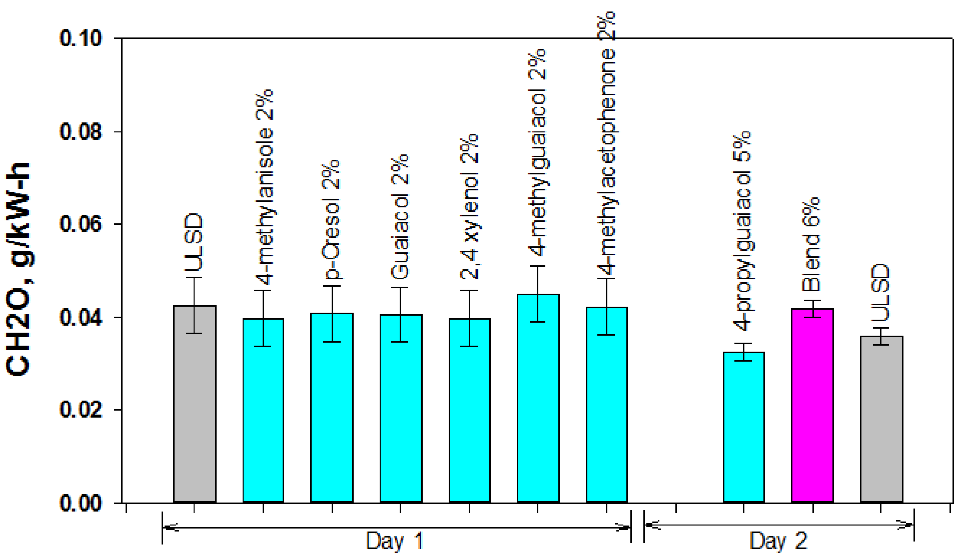


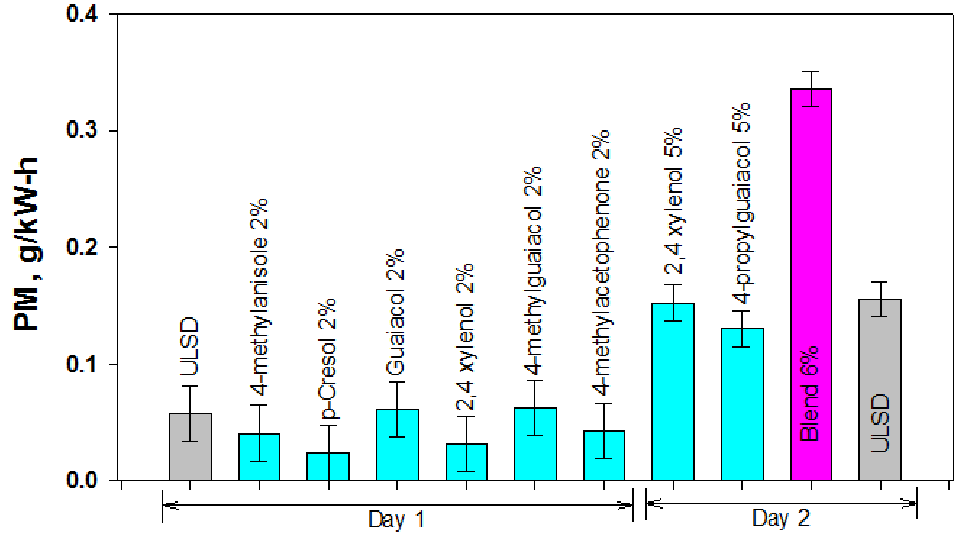


Biomass Pyrolysis Oxygenate Blends Emission Results

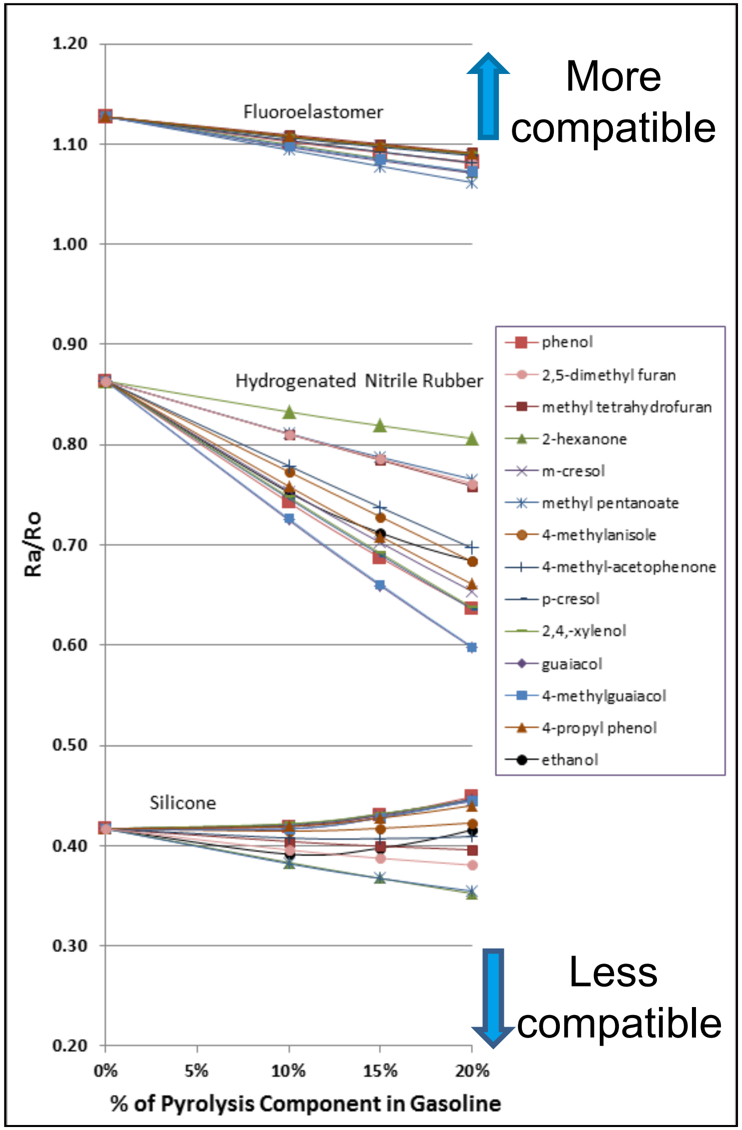
- **2% to 6% blend levels showed little measureable effect on NO_x or PM**
- **Composite blend produced a strong PM response:**
  - 2% 4-Methylacetophenone
  - 2% 4-Methylguaiacol
  - 2% 4-Propylphenol
- **No measureable effect on CH_2O**







Elastomer Compatibility – Based on Hansen Solubility Parameter



- **Relative compatibility of blends of 30% aromatic gasoline with potential pyrolysis oil components**
  - Probably worse case than diesel
- **Estimated using three-parameter Hansen solubility**
- **Ra/Ro>1 indicates limited interaction (swell) with elastomer**
- **Parameters for estimation typically not available for higher boiling – but interaction is likely to be less**
- **Fluoroelastomer shows little interaction**
- **HNR may exhibit increased swell relative to ethanol for phenolics**
- **Silicone generally poor choice**

Summary and Conclusions

- **Biomass-derived oxygenates were investigated as potential drop-in fuel components**
  - Primary focus was on performance properties of the oxygenates and their blends with conventional diesel
  - Emission effects were also measured in preliminary experiments
  - C5 ethers/esters from chemical deconstruction of biomass
  - Oxygenates from hydroprocessing of biomass fast pyrolysis oil
- **C5 molecules have good properties as drop-in diesel fuel components**
  - Additional research on properties, combustion, emissions, and the economics of manufacturing is recommended
- **Pyrolysis oxygenates are primarily high energy density phenols after hydroprocessing**
  - However, phenol and guaiacol are not desirable as drop-in fuel components because of high water solubility and likely poor solubility in hydrocarbon at higher blend levels
  - Other phenolics may be useful at low blend levels (up to 5 vol%), limited by their low cetane number
  - Additional research on fast pyrolysis oil upgrading (conversion of phenols to methyl ethers, for example), as well as fuel properties, combustion, emissions, and economics of manufacturing is recommended.

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