Performance of Biofuels and Biofuel Blends

P.I.: Robert L. McCormick
Presenter: Matthew Ratcliff

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Project ID # FT003

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Overview

Timeline

- **Project Start Date: Oct 1, 2011**
- **Project End Date: Sep 30, 2014**
- **Percent Complete: 66%**

Budget

- **Total Project Funding: $2.1M**
  - DOE Share: $1.5M
  - Contractor Share: $0.6M
- **Funding Received in FY13:** $0.7M
- **Funding for FY14:** $0.4M Planned

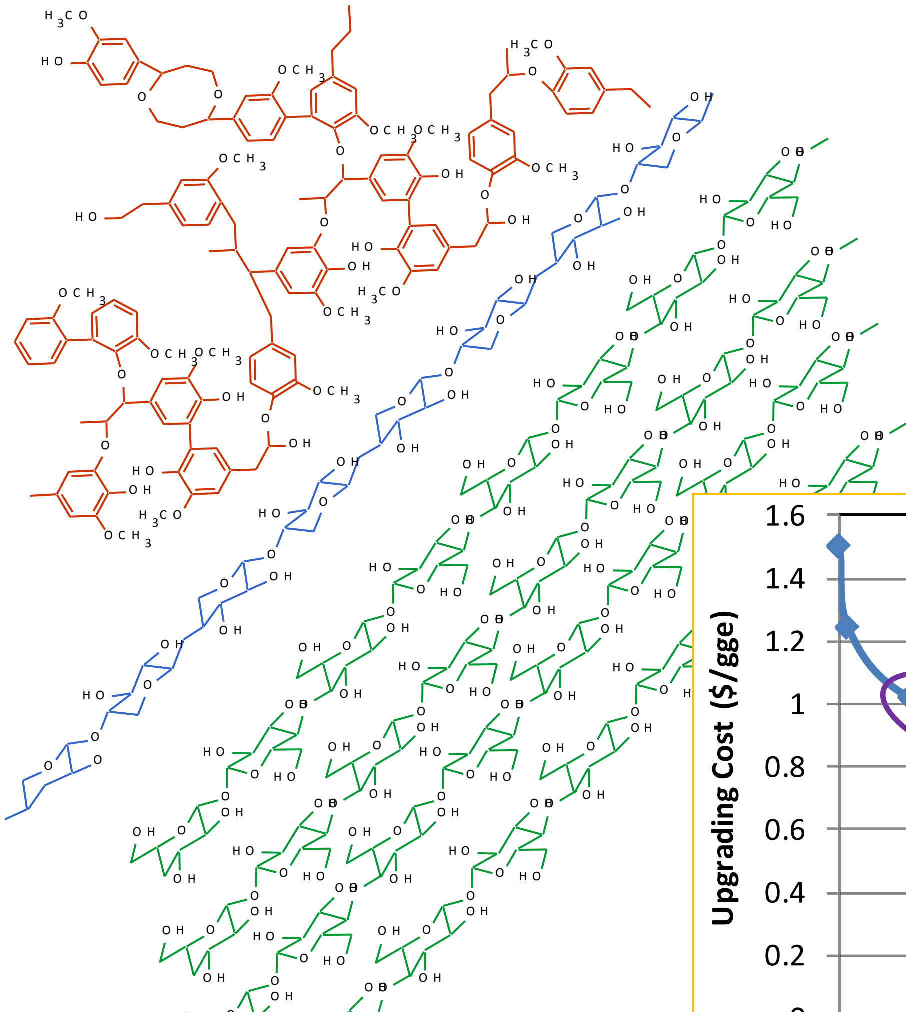
Barriers

- **Achieve >5% petroleum displacement by 2018**
  - Infrastructure compatibility
  - Cost
  - Inadequate data and predictive tools on fuel effects

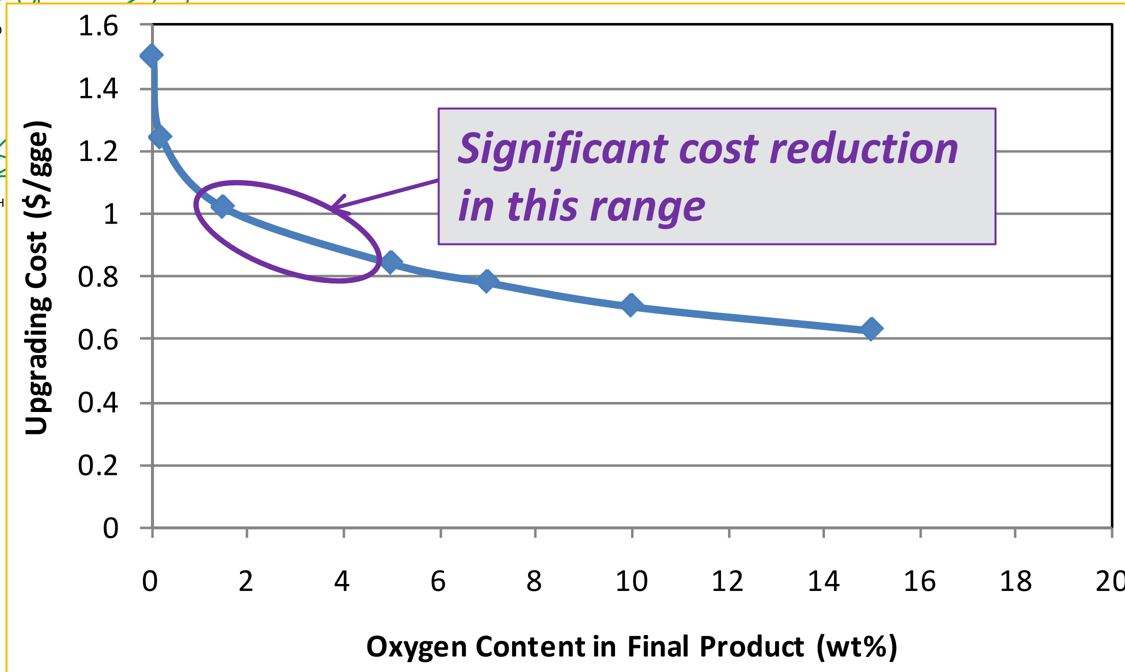
Partners

- Colorado State University (Profs. Anthony Marchese and Dan Olsen)
- Colorado Energy Research Collaboratory
- Underwriters Laboratories
- EcoEngineering, Inc. (Dr. Janet Yanowitz)
- National Bioenergy Center (NREL)
- National Advanced Biofuels Consortium (NREL)
- Project Lead: NREL

Relevance – Biomass to Hydrocarbon Biofuels?



- 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



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

Relevance – Can Oxygenate Be Tolerated in Drop-in Fuel?

- **Article of faith that "drop-in" fuels are hydrocarbon**
  - Compatible with engines
  - Compatible with fuel distribution (pipeline) and refueling infrastructure
  - Fungible (interchangeable)
- **Can economics be improved if less than 100% of the oxygen is removed?**

Determine if and at what levels biomass-derived oxygenates are scientifically and commercially feasible in drop-in fuels

- **Past year's work focused on:**
  - *Properties of biomass-derived oxygenate blends with diesel and gasoline*
  - *Diesel engine performance and emissions*

Milestones

Month/ Year	Milestone or Go/No-Go Decision	Description	Status
12/2013	Milestone	Deliverable: Complete property testing of oxygenate blends	Complete
6/2014	Milestone	Deliverable: Set up GDI engine system for fine PM measurements and initiate testing	On schedule
9/2014	Milestone	Deliverable: Complete diesel engine testing of oxygenate blends	On schedule
9/2014	Milestone	Deliverable: Complete GDI engine testing of oxygenate blends	On schedule

GDI = gasoline direct injection
PM = particulate matter

Approach/Strategy

- Use reagent grade oxygenates from chemical suppliers
- Measure properties of the neat oxygenates
- Prepare blends with conventional diesel and gasoline
    - Fuel property testing (ASTM standards and stability)
    - Modeled material compatibility (Hansen solubility)
    - Diesel emission studies (regulated plus some toxics)
    - Diesel durability (300 hr., small stationary engine)
    - GDI particle number (PN) emissions from aromatic oxygenates
- Research addresses barriers of infrastructure, cost, and fuel effects on properties and performance


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Photo: Mike Lammert, NREL


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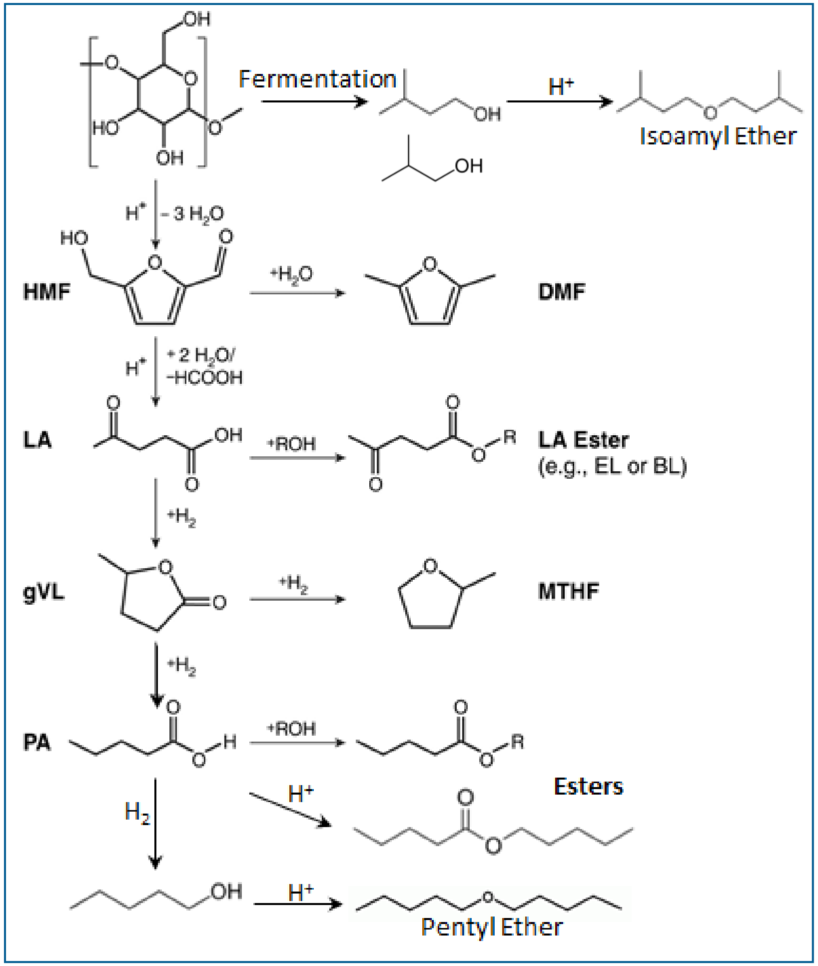
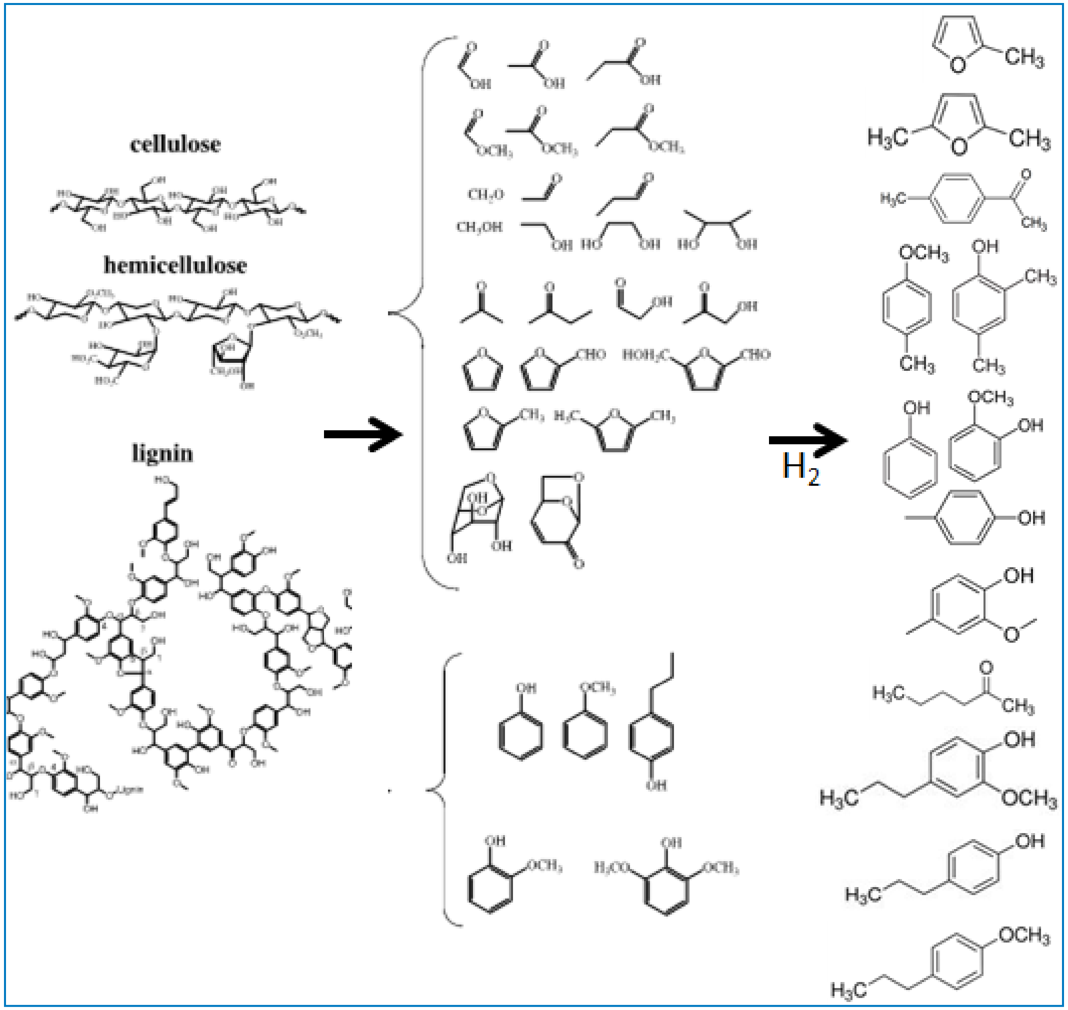
Approach/Strategy – II

Acid Deconstruction



Blending components from chemical deconstruction of biomass – tested at 10 to 15 wt%

Fast Pyrolysis-Hydroprocessing

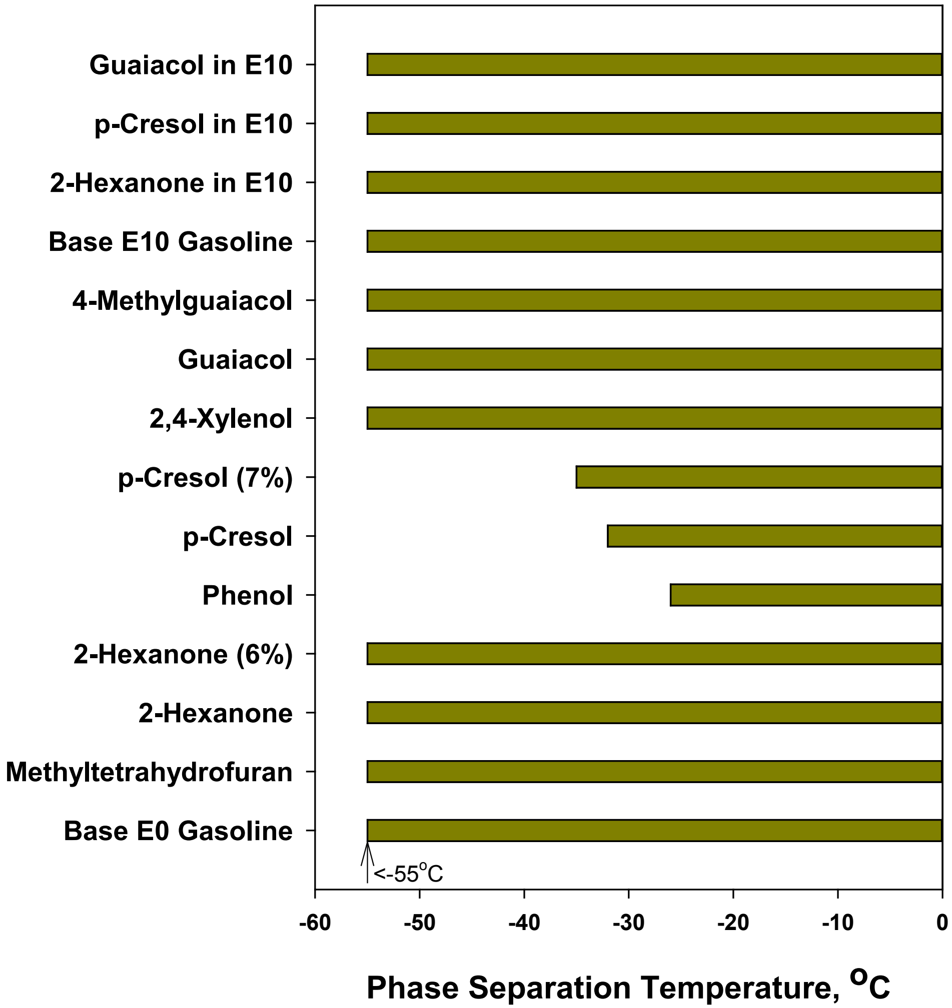


Residual that remains after hydroprocessing of a bio-crude (such as fast-pyrolysis oil) – tested at 2 or 3 wt%

Technical Accomplishment – Gasoline Properties

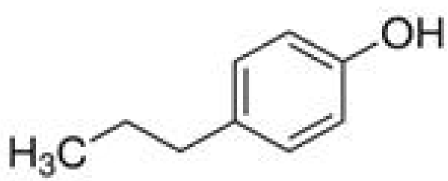
- **Oxygenates blended into summer suboctane blendstock**
- **All tested oxygenates except MTHF increased gasoline octane number**
- **Most oxygenates boiled near or above the T90 of gasoline**
- **No effects on:**
  - Distillation curve
  - Reid vapor pressure
  - Oxidation stability (ASTM D525)
  - Copper corrosion
  - Silver corrosion
- **Phase separation temperature increased for phenol, cresol**
  - But not for xylenol and guaiacol
  - Effect is mitigated in 10% ethanol blends

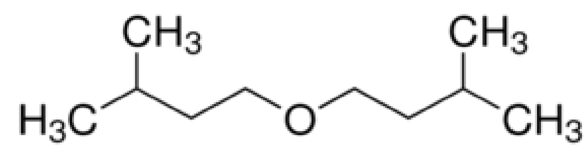
Residual oxygenates tested at nominally 2 or 3 wt% unless noted

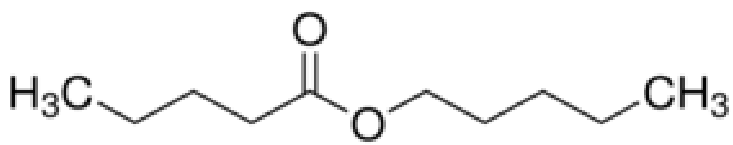


Technical Accomplishment – Diesel Properties

- **Oxygenates tested at 2 or 3 wt% unless noted**
- **Blended with certification diesel**
- **No effects observed for:**
    - Cloud point (-30°C)
    - Copper corrosion
    - Thermal stability (ASTM D6468)
    - T90
    - Flashpoint







- **Phenolic compounds improved lubricity**
- **No incompatibility with B5**
- **Aromatic oxygenates have very low cetane number (CN)**
- **Di-isoamyl ether (CN=96) increased CN by 5 at 20 wt%**
- **Pentyl pentanoate (CN=30) decreased CN by 1 at 10 wt%**

Technical Accomplishment – Storage Stability

Gasoline

- **Gum formation assessed by ASTM D873 (potential gum)**
- **2-Hexanone increased gum formation at higher blend levels (6 wt% oxygenate)**
  - 64 mg Gum/100 mL vs. 20 for control
- **Dimethyl furan (DMF) caused a dramatic increase in gum formation**
  - 713 mg Gum/100 mL vs. 20 for control
  - Unknown mechanism of polymerization

Follow up investigation of DMF and other furanics storage stability recommended

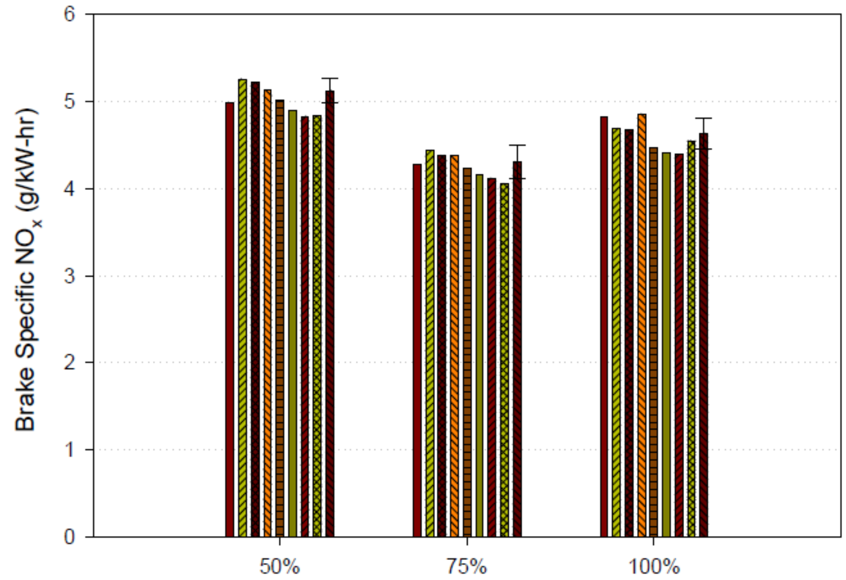
Diesel

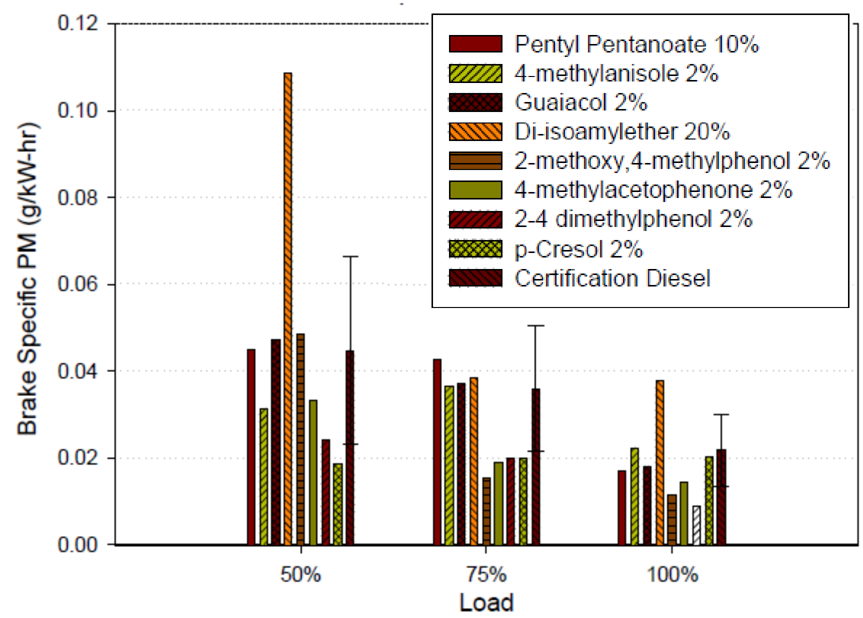
- **Oxidation Stability (ASTM D2274)**
  - Typical pipeline specification is <2.5 mg Insoluble/100 mL
- **Ketone (acetophenone) has well-known polymerization mechanism (aldol condensation)**
- **No significant increase in insolubles in testing to date**
- **Additional work ongoing**

Technical Accomplishment – Diesel Emissions

- **Eight oxygenates blended with certification ULSD fuel**
- **John Deere PowerTech Plus (4.5L)**
  - Turbocharged, common rail injection
  - Tier 3 emissions certification (173 hp)
- **No significant effects on CO, NO_x, total hydrocarbons, or formaldehyde**
- **Low PM emission level and large error bar suggest no significant change in PM**
  - Current experiments following up on apparent PM effect of di-isoamyl ether

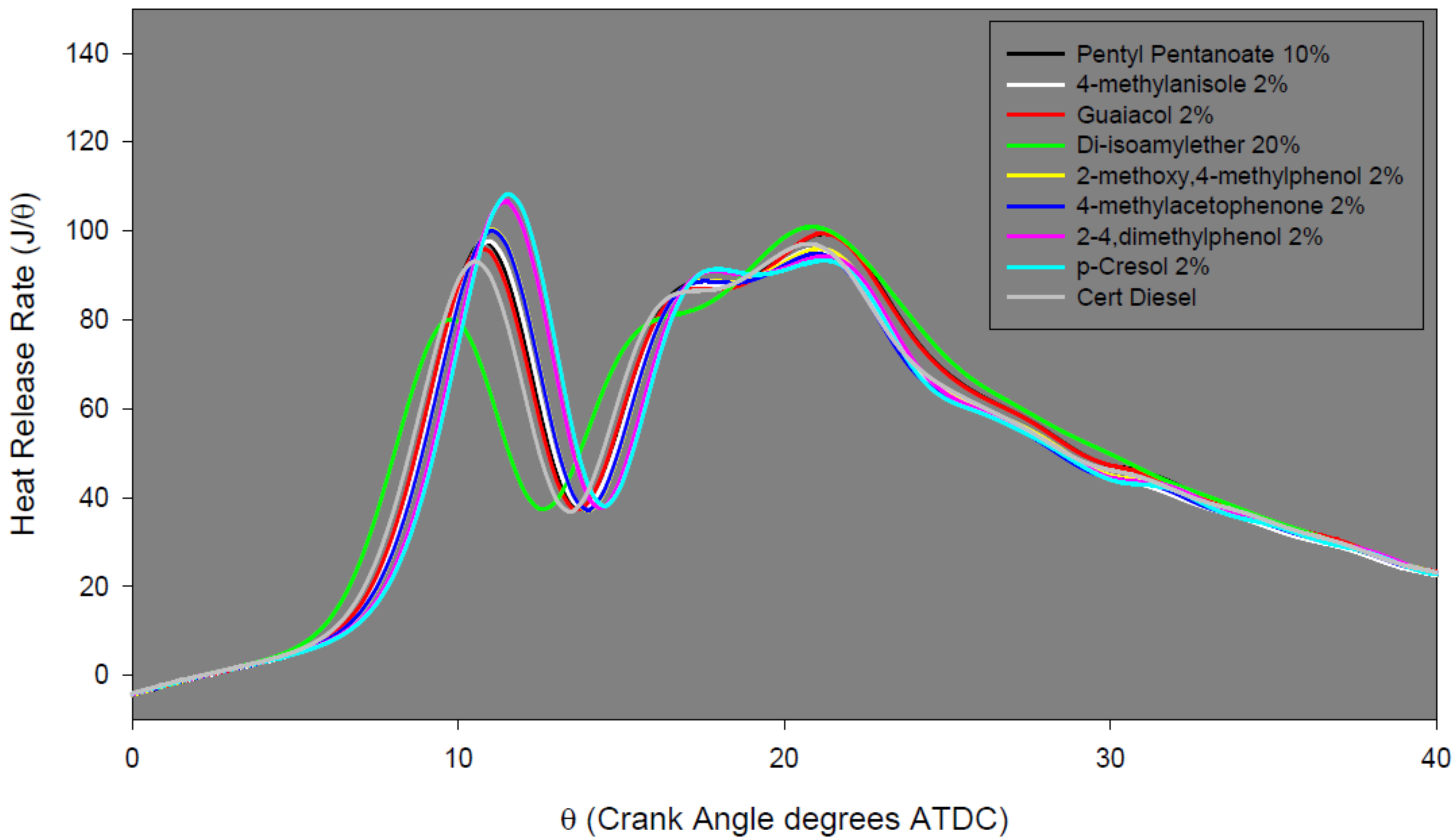
ULSD = ultralow sulfur diesel





Technical Accomplishment – Diesel Combustion Analysis

- **Relative to certification diesel:**
  - Low CN oxygenates show longer ignition delay, greater premixed burn fraction
  - Di-isoamyl ether (CN=96) reduced ignition delay and premixed burn fraction



Responses to Previous Year Reviewers' Comments

"the work of this team is essential to find and fix the problems that biofuels can create, or to capitalize on benefits of biofuels" *The research team greatly appreciates this positive comment.*

"The reviewer applauded the very impressive range of activities, and suggested than an integration of these activities would be very valuable in illustrating the impact of this project on addressing the technical barriers" *We continue with a broad range of activities, but agree than integration is important. The current activity on drop-in fuel oxygenates has made substantial progress at integration of fuel properties, handling, combustion, and emissions.*

"The reviewer mentioned the concept of only removing some of the oxygen from the bio-derived fuel components, but concluded that it will need to be thoroughly tested to evaluate impacts on emissions and engine systems, and on the performance, durability, and materials compatibility of aftertreatment systems" *The objective of the drop-in fuel oxygenates project is to begin this thorough testing process.*

Collaboration and Coordination with Other Institutions

- Colorado State University (Profs. Anthony Marchese and Dan Olsen)
  - University subcontractor
  - Performing diesel emissions and durability testing
- Colorado Energy Research Collaboratory
  - Provider of co-funding for CSU
- Underwriters Laboratories
  - Informal collaboration on materials compatibility
  - Not-for-profit testing laboratory
- EcoEngineering, Inc. (Dr. Janet Yanowitz)
  - Subcontractor/consultant
  - Data analysis, literature review and theoretical calculations
- National Bioenergy Center (NREL)/National Advanced Biofuels Consortium (NREL)
  - Organizations within NREL (federal laboratory) – not Vehicle Technologies Office - funded
  - Informal collaboration on oxygenates produced from biomass

Remaining Challenges and Barriers

- A more complete understanding of the chemical composition of residual oxygenates in hydrotreated pyrolysis and hydrothermal liquefaction bio-oils
- Investigation with a mixture of oxygenates simulating that present in actual hydroprocessed samples
- Understanding the underlying mechanism for gum formation in dimethylfuran blend and how this applies to other candidate biofuels
- Biomass-derived oxygenate impacts on toxic emissions from more advanced engines – both spark ignition and direct injection
- Particle number emission impacts of gasoline boiling range oxygenated aromatics in GDI engine

Proposed Future Work (FY14)

- **GDI Engine Study**
  - GDI engines can have high particle number (PN) emissions (correlated with fuel aromatics)
  - Most biomass-derived oxygenates are aromatics
    - Very high research octane number (RON) (>130) methylanisole, cresol, dimethyl furan
    - Does oxygen on or in the aromatic ring mitigate the impact on PN?
  - GDI single cylinder engine with Dekati diluter and Fast Mobility Particle Sizer (FMPS) particle analyzer
  - *PN results are critical DOE milestone due in September*
- **Diesel Engine Durability Study**
  - Examine diesel oxygenates (including a mixture of residuals) in short (300 hr.) durability test
  - Examine effects on engine lubricant and fuel injector deposits
  - Includes testing of “cocktail” of oxygenates

Proposed Future Work (FY15 and beyond)

- Study gum formation with furanics in gasoline
- Research potential stability issue in diesel
- Obtain better data on residual oxygenates in py-oil and other bio-oils – especially diesel fraction
- Measure fuel properties using actual hydroprocessed biomass materials
- Measure properties of actual biomass-derived oxygenate blend components to examine impurities
- Expand studies of emissions and emissions durability
- Test fuel injection system compatibility and durability

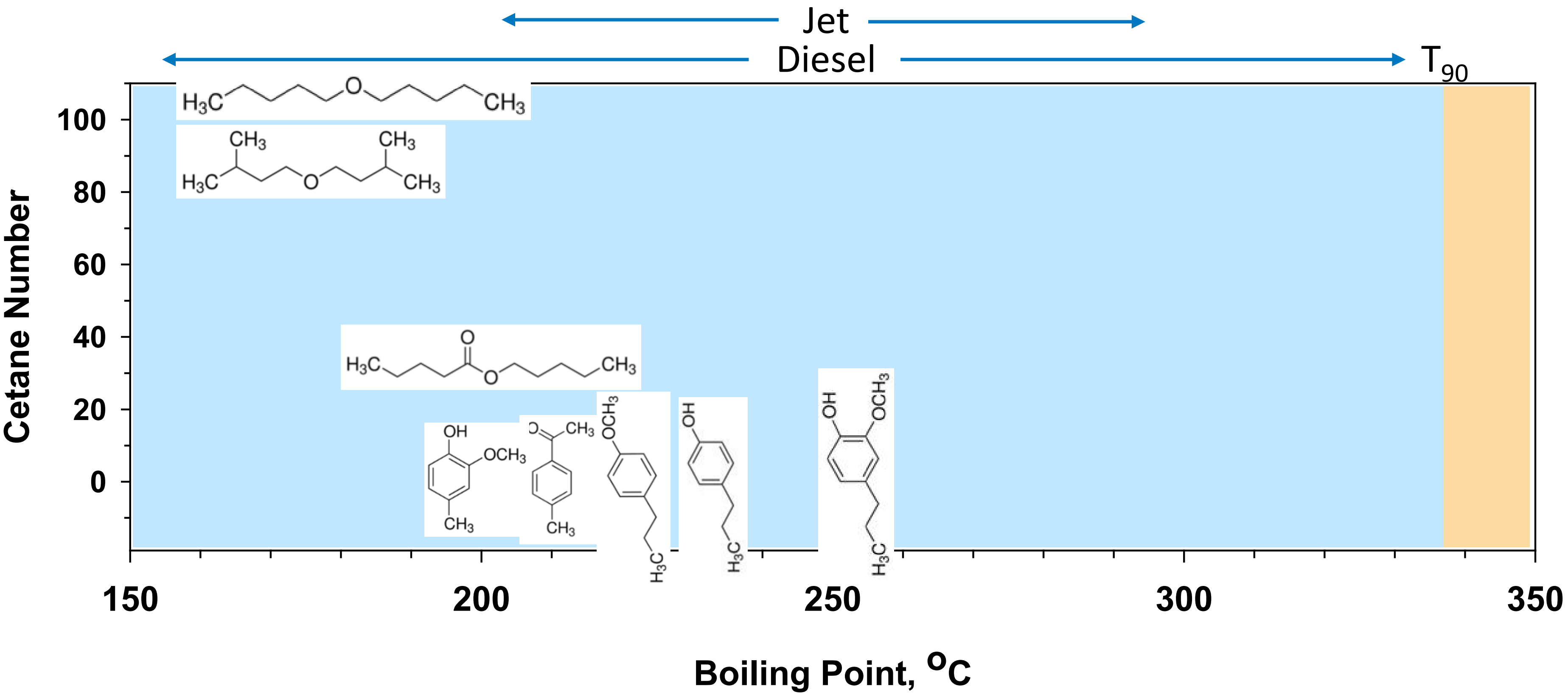
Summary

- **Gasoline**
  - Phenol and cresol probably not suitable drop-in fuel components
    - Poor solubility in hydrocarbon
    - Corrosivity
  - DMF may undergo polymerization
    - Unknown mechanism – potentially solved by antioxidants?
  - Other oxygenates performed well in gasoline (isobutanol, hexanone, methyl pentanoate, methyl anisole, xylenol, guaiacol)
    - Methyl guaiacol and acetophenone potentially have too high a boiling point
- **Diesel**
  - Residual pyrolysis oxygenates reduced CN but had no effect on other diesel properties
  - Di-isoamyl ether and pentyl pentanoate appear to be suitable blend components (CN of pentyl pentanoate is 30)
  - Preliminary results show no impact on emissions
- **Elastomer compatibility**
  - Theoretical calculations predict less effect than ethanol on elastomer swell

Technical Back-Up Slides

Biomass-Derived Diesel Oxygenate Boiling Points

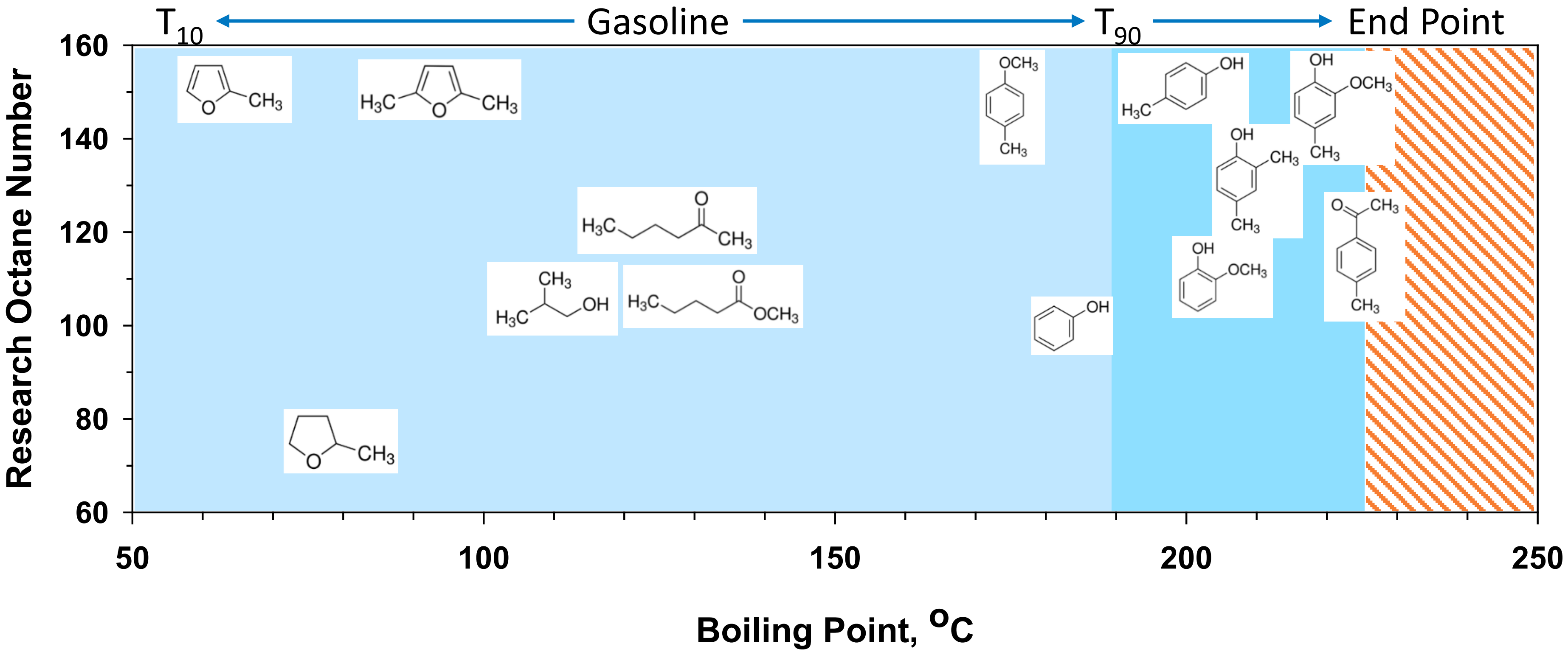
- High CN pentyl-ethers plus pentyl valerate from acid deconstruction and upgrading chemistry
- Pyrolysis-derived oxygenates are low CN aromatic compounds



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

Biomass-Derived Gasoline Oxygenate Boiling Points

- Phenol is undesirable in fuels because of its poor solubility in hydrocarbon, high solubility in water, and corrosivity
- From acid deconstruction and upgrading chemistry, furans, methyl pentanoate, hexanone and isobutanol are of interest because of high RON
- Pyrolysis-derived oxygenates, other than methyl anisole, are high RON aromatics but boil above the T_{90} of gasoline limiting applicability



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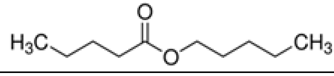
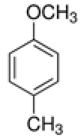
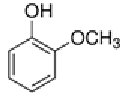
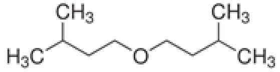
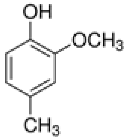
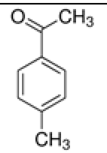
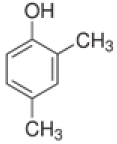
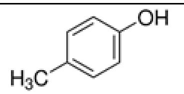
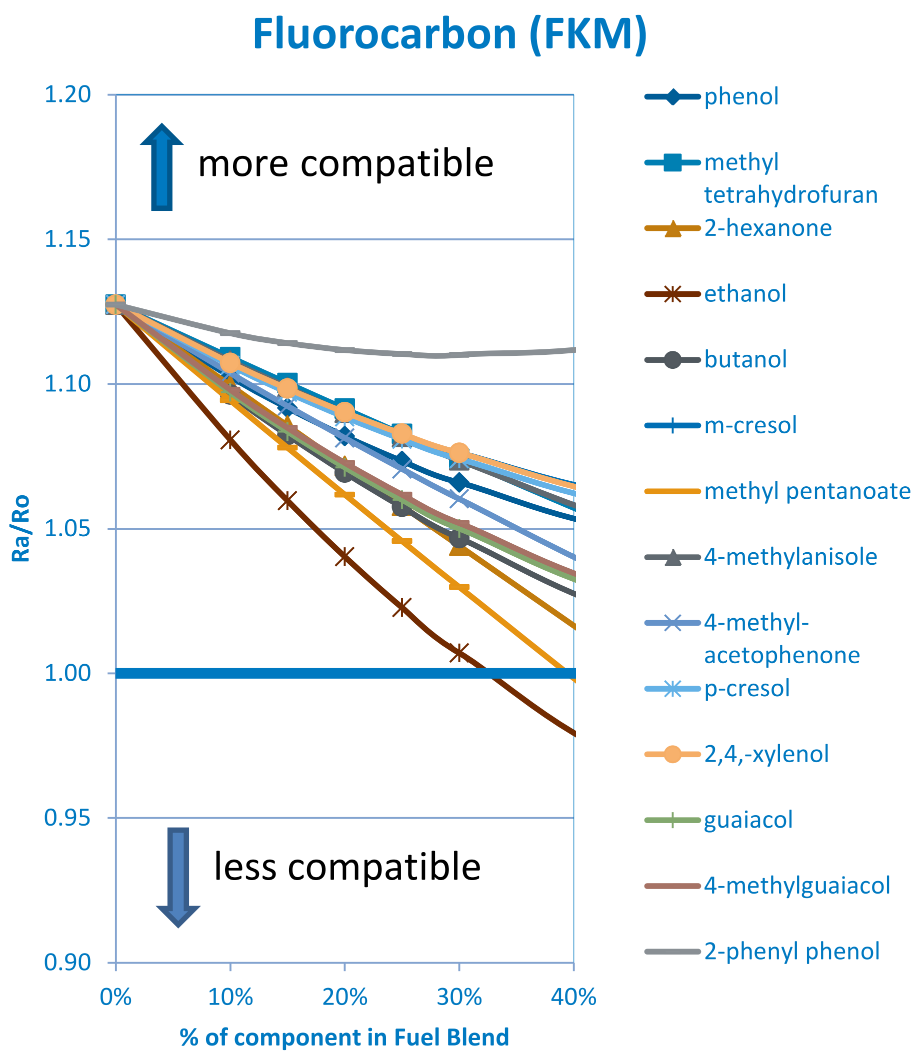
Technical Accomplishment – Diesel Emissions

- **Diesel emissions testing was performed on 8 different oxygenate components blended with certification ULSD diesel.**
- **Tests were performed using a 4-cylinder, turbocharged, 4.5-L John Deere PowerTech Plus common rail, DI diesel engine that meets Tier 3 emissions specifications.**
- **Gaseous emissions measurements included CO, CO_2, NO, NO_2, and total hydrocarbons. Particulate measurements included total PM mass emissions, particle size measurements, and elemental-to-organic carbon ratio.**
- **In-cylinder pressure measurements were used to calculate apparent rate of heat release.**

Blending Component	% by Volume in Certification Diesel	Specific Gravity	Viscosity (cSt)	Derived Cetane Number	Net Heating Value (kJ/kg)	Molecular Structure
Pentyl pentanoate	10	0.8576	2.30	42.2	44,536	
4-methylanisole	2	0.8586	2.43	41.5	45,417	
Guaiacol	2	0.8614	2.67	41.6	45,119	
Di-isoamylether	20	0.8411	2.01	47.3	44,817	
2-methoxy,4-methylphenol	2	0.8608	2.48	41.2	45,070	
4-methyl-acetophenone	2	0.8593	2.46	41.6	45,234	
2-4, dimethylphenol	2	0.8594	2.48	40.2	45,210	
p-Cresol	2	0.8597	2.51	40.3	45,211	
2007 Certification ULSD	-----	0.8565	2.80	45.0	45,531	

Technical Accomplishment: Elastomer Compatibility

- **Example:**
  - Results for FKM
  - Relative compatibility of blends of 30% aromatic gasoline with potential pyrolysis oil components
- **Estimated using three-parameter Hansen solubility**
- **Ra/Ro>1 indicates limited interaction (swell) with FKM**
- **Effects of biomass-derived oxygenates less than for ethanol**
- **Several other common automotive fuel system elastomers also investigated**



Projects Not Covered in Presentation

- **Quality Specifications and Test Methods**
  - Leading ASTM update of ethanol-gasoline test methods
  - Updating 10-year-old *Compendium of Pure Component Cetane Number Data*
  - CRC DP-05-12 *The Effect of Wax Settling and Biodiesel Impurities on Light-Duty Diesel Performance*
- **Biodiesel Compatibility with Advanced Emission Control Systems**
  - Primary funding (80%) under CRADA with National Biodiesel Board
  - Collaboration with Oak Ridge National Laboratory
  - Effect of biodiesel residual metals in biodiesel on emission control components
- **Characterization of High Knock Resistant Fuel Blends**
  - Measurement of heat of vaporization, RON, and other factors important for knock resistance
  - Focus on high-RON biomass-derived oxygenates (isobutanol, methyl anisole, dimethyl furan)
- **Nucleation of Saturated Monoglycerides (SMG) from Biodiesel Blends at Cold Temperatures**
  - Understanding fuel composition (including petro-diesel) factors on crystallization of SMG
  - SMG are the main component in biodiesel responsible for cold weather issues