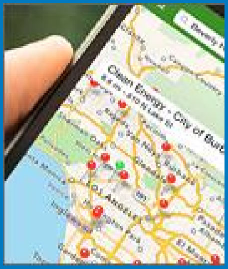
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Performance of Biofuels and Biofuel Blends



P.I.: Robert L. McCormick
Collaborating Researchers:
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June 11, 2015

Project ID # FT003

Overview

Timeline

- **Project Start Date: Oct 1, 2014**
- **Project End Date: Sep 30, 2017** (assuming 3 year AOP)
- **Percent Complete: 25%**

Barriers

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

Budget

- **Total Project Funding: $2.0M** (assuming 3 year AOP)
- **Funding in FY14:** $0
- **Funding in FY15:** $0.67M

Partners

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

Relevance and Project Objective

- **Addressing barriers to achieving >5% petroleum displacement using conventional and advanced biofuels by 2018**
  - Infrastructure compatibility
  - High cost of fuels
  - Inadequate data and predictive tools on fuel performance
- **Conventional biofuels (ethanol, biodiesel and RD)**
  - Supporting development of ASTM standards
  - Addressing OEM concerns
  - National Biodiesel Board CRADA
- **Advanced cellulosic biofuels – *primary focus in FY15***
  - Properties of biomass oxygenates (precursor to ASTM)
  - Impact on emissions (diesel and GDI)
  - Knock resistance of high octane oxygenates

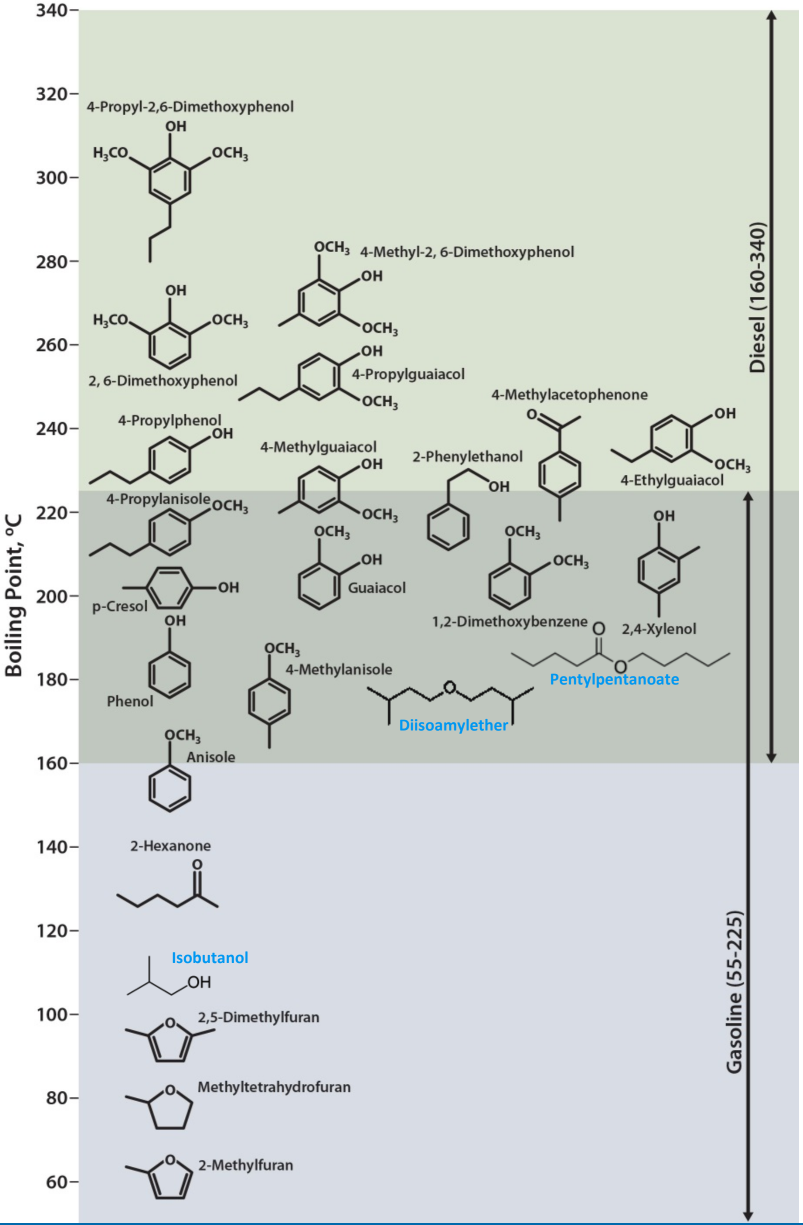
Approach

- **Conventional Biofuels**
  - Utilizing commercially produced samples
  - Focused on research to address issues brought up at ASTM and CRC as critical issues
- **Advanced Cellulosic Biofuels**
  - Seeking collaborations with producers to provide product samples
    - Utilizing reagent or technical grade material from chemical suppliers if actual product not available
  - Fuel property testing (ASTM standards and stability)
  - Modeled material compatibility (Hansen solubility)
  - Diesel emission studies (regulated plus some toxics - CSU)
  - Diesel durability (300 hr., small stationary engine - CSU)
  - GDI particle number (PN) emissions from aromatic oxygenates
  - GDI knock limited spark advance
- **Quarterly milestones to demonstrate subtask completion and results write up (see backup slides)**

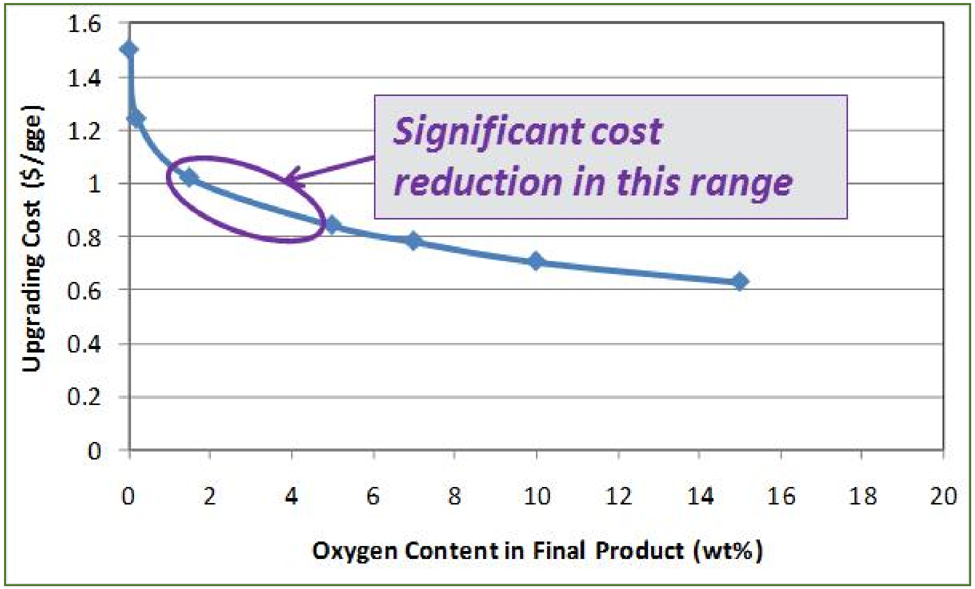
Summary of Conventional Biofuels R&D

- **National Biodiesel Board CRADA (funding 80% NBB/20%DOE)**
  - Initiated July 2005, several $million funds-in over 10 years
  - Impact of residual metals on emission control catalysts (Na, K)
    - Collaboration with Cummins, ORNL, MECA, EMA
    - 1000 hr accelerated aging of HD system completed FY14
    - Used catalyst evaluation at Cummins and ORNL ongoing
  - B20 oxidation stability on-board LD vehicle
    - Collaboration with Volkswagen, Mercedes, GM, EMA
    - Four VW Passat tested on dyno (hot test cell, hot fuel), and then further aged at VW proving ground in Arizona for several months
    - B20 at ASTM spec level of stability and a higher level
    - Car testing completed, fuel analysis and data analysis ongoing
- **SMG effects on Bxx cold weather performance**
- **Detailed property assessment and literature review of butanol gasoline blends – including heat of vaporization, viscosity, …**

Why biomass oxygenates? Why not hydrocarbon?



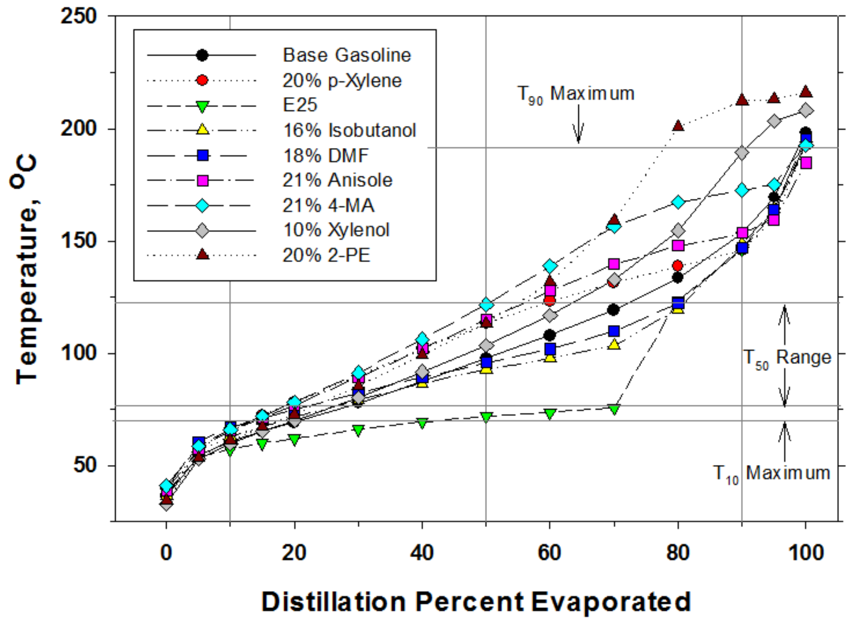
- Biomass has high oxygen content:
  - 40 to 60 wt%
  - Molar O/C about 0.6
- Economically rejecting all oxygen may not be possible
- Can oxygenates be drop-in fuels?
- Oxygenates identified from:
  - Partially hydrotreating biomass pyrolysis oil
  - Chemical conversion of biomass carbohydrates
  - Biochemical conversion (isobutanol)



Measured Oxygenate Effect on GDI Engine PM Emissions-I

Compound	Boiling Point (°C)	Blending RON and MON	Vapor Pressure, 443K (kPa)	DBE
Ethanol	78	110, 90	1545	0
Isobutanol	108	106, 90	596	0
2,5-Dimethyl-furan	94	129, 99	538	3
Anisole	154	117, 98	153	4
4-Methyl-anisole	174	139, 108	87.7	4
2,4-Xylenol	211	179, 146	30.3	4
2-Phenyl-ethanol	220	127, 103	21.5	4

Oxygenates blended with 88 RON summertime BOB at 10 to 20 vol%



Particulate Matter Index (PMI):

$$PMI = \sum_{i=1}^{n} \left[\frac{(DBE_i + 1)}{VP(443K)_i} \times Wt_i \right]$$

Where-

$$DBE = (2C + 2 - H)/2$$

Wt_i = *Weight fraction of compound*

VP = *Vapor pressure at 443K (170°C)*

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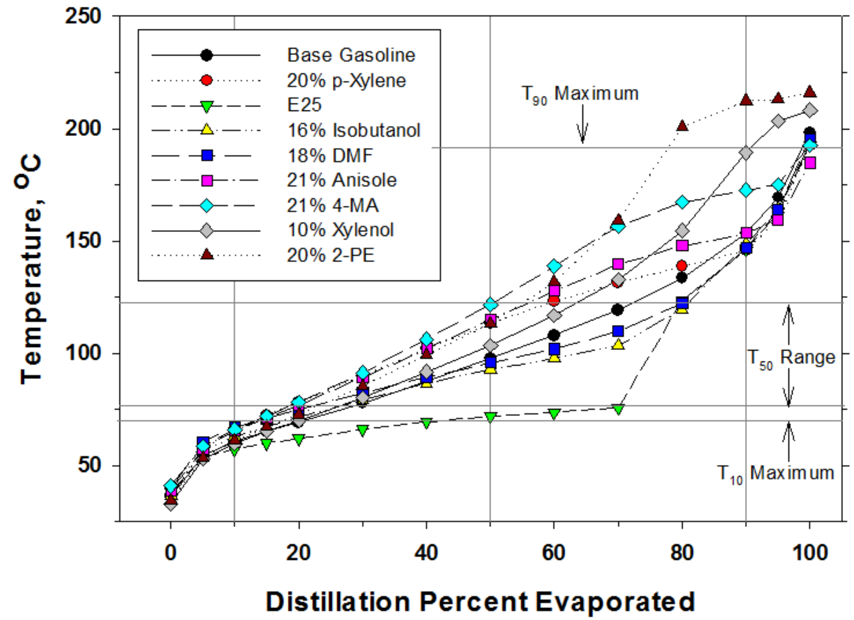

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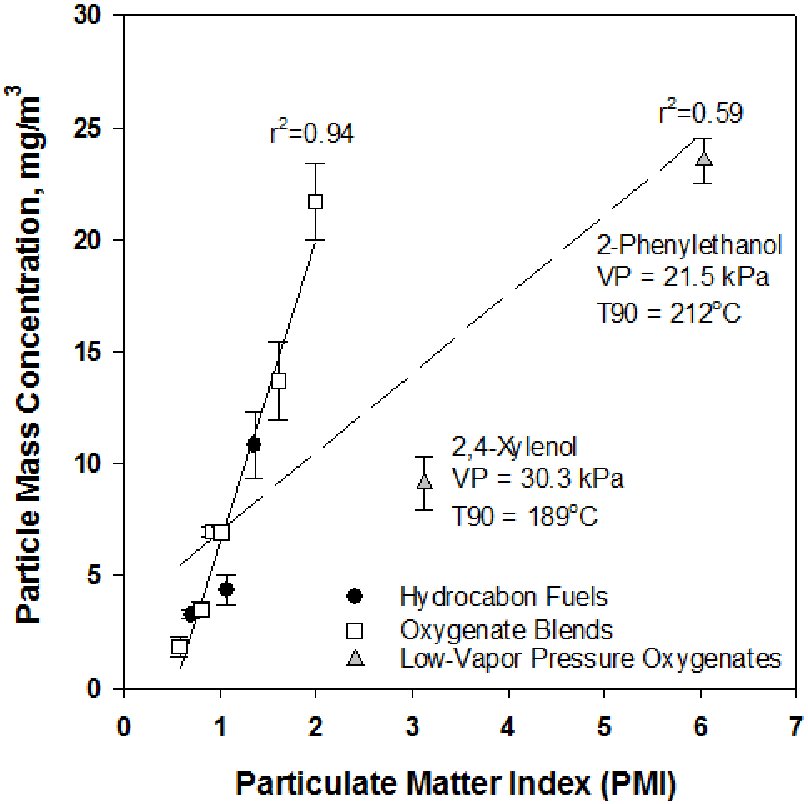
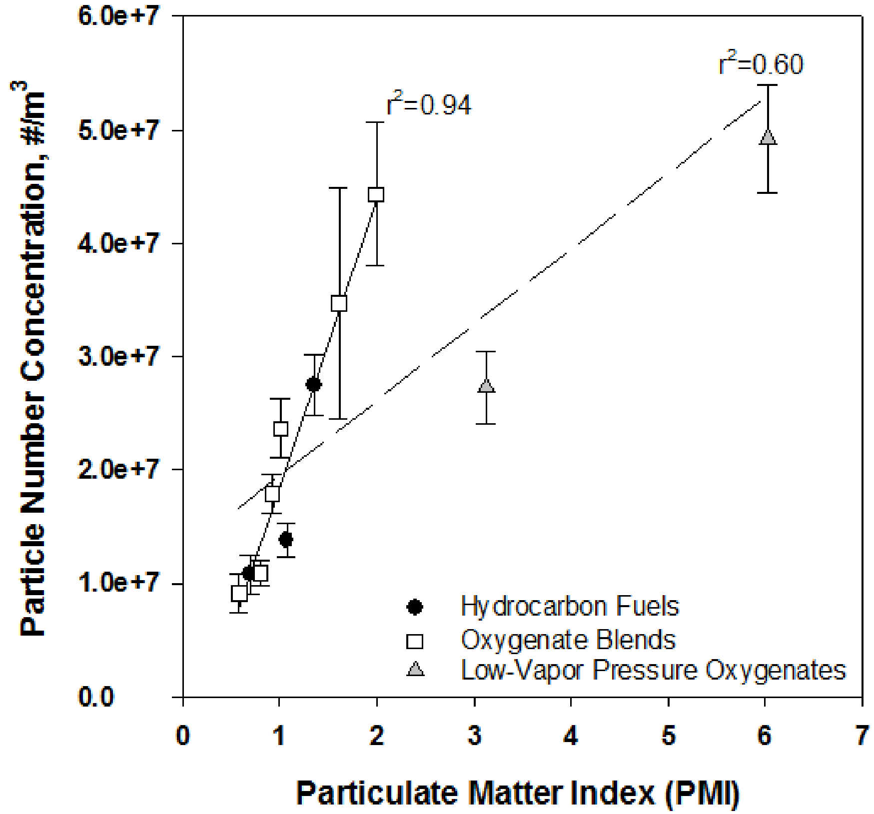
Measured Oxygenate Effect on GDI Engine PM Emissions-II

- PMI correlates with PM-mass and number for most fuels
- Fuels falling away from the trend are very low vapor pressure and do not appear to completely burn (end up in lube oil) – failing gasoline T90
- Suggests no impact of fuel oxygen on PM – to be confirmed in future experiment



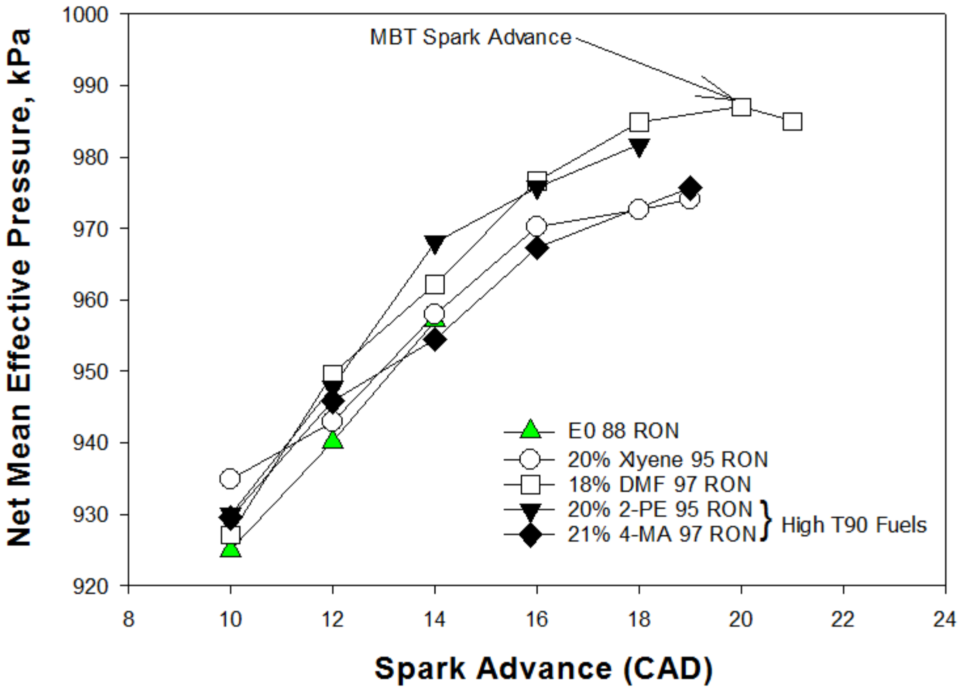
AVL Micro-soot sensor and dilution system for PM

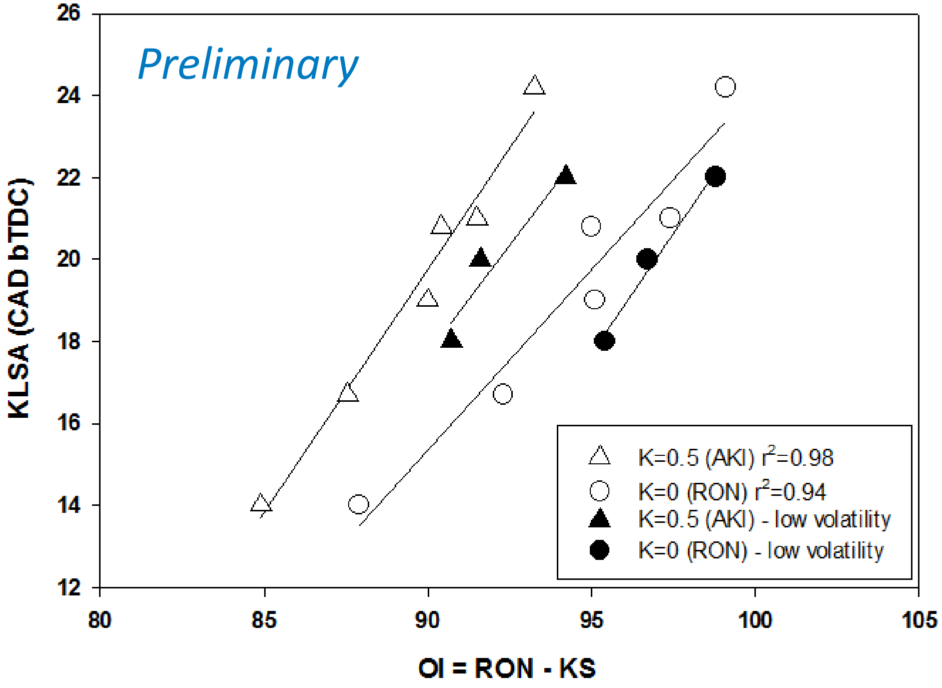


TSI Fast Mobility Particle Sizer (FMPS) w/ Dekati diluter & thermodenuder for PN

Measured Knock-Limited Spark Advance for High Octane Biomass Oxygenates

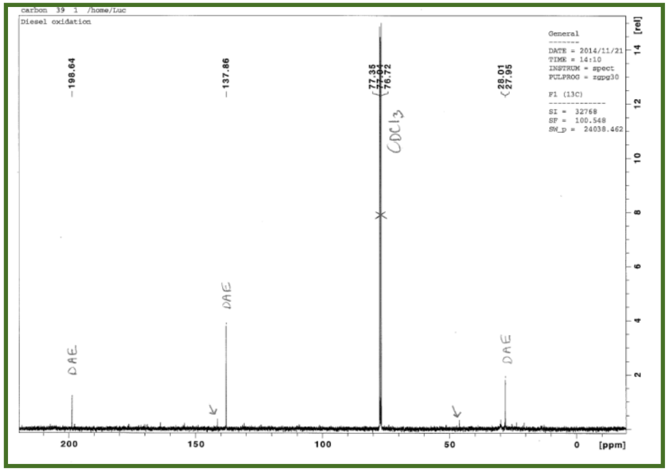
- **Spark sweeps conducted at fixed load: 1500 rpm, nominal 980 kPa NMEP**
  - Very knock limited condition for 88 RON base gasoline
  - Even 95 RON blend could not reach MBT but K is clearly greater than zero
- **Knock integral = 10 defines KLSA**
- **AKI or RON correlate well with KLSA for normal volatility fuels**
- **Fuels failing T90 or having high boiling temperatures over the full range above T50 "underperform" for knock resistance**

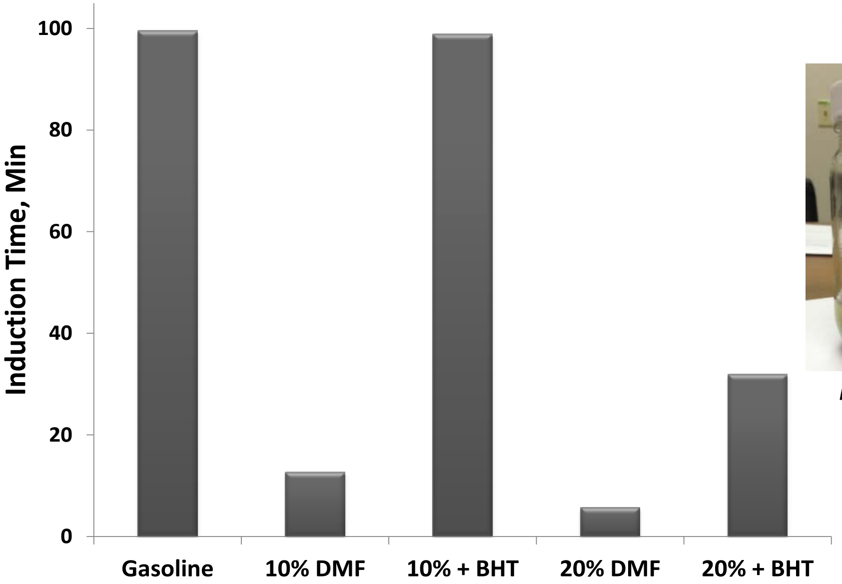




Revealed Mechanism for DMF-Gasoline Blend Oxidative Degradation

- **Hundreds of published studies on combustion of DMF**
  - Promising biomass-derived high octane compound
- **DMF blends with gasoline show high levels of insoluble gum formation on D873 test**
  - 100°C/100 psi O_2 for 16 hr
  - 600 to 800 mg/100 mL – much higher than base gasoline
  - Also failed gasoline stability test D525
  - No prior reports of this reaction occurring
- **^{13}C NMR indicates gum is largely 2,5-hexenedione (aka diacetylethylene or DAE)**
  - Melts 5°C, very water soluble
  - Poorly soluble in hydrocarbon
- **Evidence of DMF oxidation**
  - ASTM method D7525 140°C, 72.5 psi O_2
  - 10% pressure drop defines induction time
  - DMF in isooctane under O_2 and N_2
  - With N_2 no break in 18 hours
  - 1,000ppm BHT increased stability

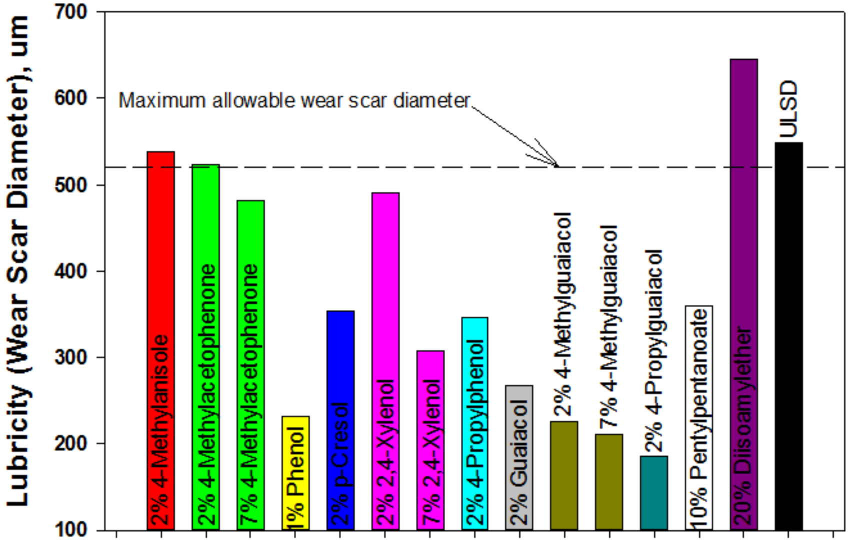


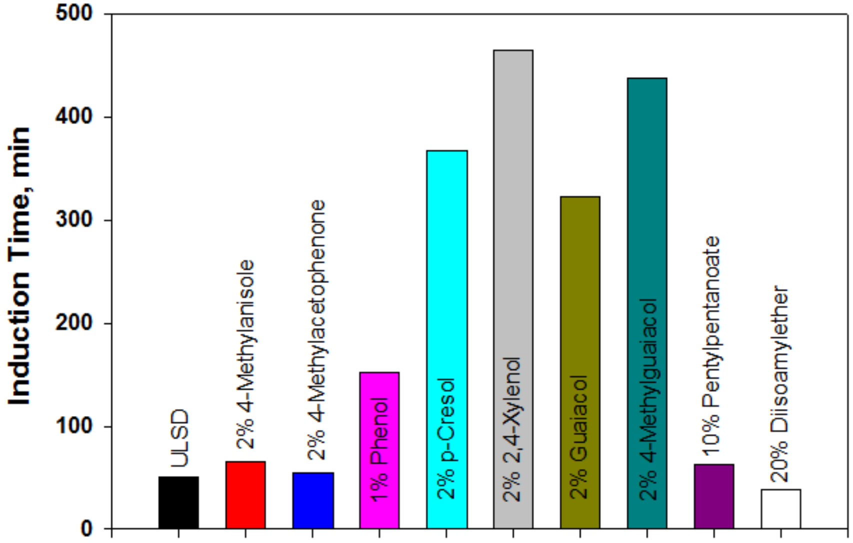


NREL 32488

Diesel Oxygenate Fuel Property Impacts

- **Emission results presented last year**
- **New results: completed property testing**
- **Lubricity**
  - Significantly improved by ester and phenolics
  - Unaffected or degraded by ether and ketone
- **Oxidation stability**
  - ASTM D7545 (RSSOT)
  - Phenolics act as antioxidants
  - No peroxide, acid, or insoluble formation on D4625 12 week test
- **Thermal stability**
  - ASTM D6468
  - No effect of any oxygenates (reflectance >80% in all cases)





Responses to Previous Year Reviewers' Comments

"The reviewer asked what the fate of the furanics (tailpipe emissions), and said that the project will be looking at these questions, but will need to be aware of the analytical challenges." *The terms dioxins and furans are commonly used to refer to a family of toxic chemicals that includes the polychlorinated dibenzo dioxins, the polychlorinated dibenzofurans (PCDFs), and the polychlorinated biphenyls. We believe the reviewer may have been referring to these, which will not be produced in an engine. Future work will include unregulated emission impacts.*

Several reviewers noted the need for expanded industry involvement, especially from biofuel producers, and the need to test real pyrolysis-derived fuels. *We agree with these comments and have reached out to industry and other national lab partners engaged in biomass conversion. Adequate quantities of pyrolysis biofuel are not available in FY14/FY15, but may be available in FY16/FY17 (collaboration with projects at NREL and Pacific Northwest National Laboratory [PNNL]). Results of this work have also been presented to the USCAR and U.S. DRIVE Fuels Working Groups.*

"The reviewer mentioned that the project will explore some very interesting impacts of oxygen location in cyclic compounds on PM, and that it will explore impact of furanics on gum formation." *Research presented here demonstrates that we have followed through on these interesting activities.*

Collaboration and Coordination with Other Institutions

Conventional Biofuels

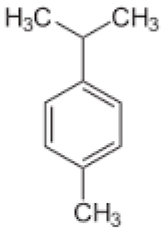
- Cummins
- Engine and Truck Manufactures Association
- GM
- Manufacturers of Emission Controls Association
- Mercedes
- National Biodiesel Board
- ORNL
- Renewable Fuels Association
- Volkswagen

Advanced Cellulosic Biofuels

- Colorado State University (Profs. Anthony Marchese and Dan Olsen)
  - Diesel emissions and durability testing
- Colorado Energy Research Collaboratory
  - Cost sharing (co-funding to CSU)
- EcoEngineering, Inc. (Dr. Janet Yanowitz)
  - Data analysis, literature review and theoretical calculations
- Eindhoven Technical University - Netherlands (Dr. Michael Boot)
  - Oxygenate ignition chemistry
  - Hosted PhD student Miao Tian at NREL
- NREL and PNNL
  - Informal collaboration on oxygenates produced from biomass
- Underwriters Laboratories
  - Materials compatibility

Proposed Future Work

- **Complete biodiesel metals and oxidation stability projects, publish results**
- **Determine if gel formation on fuel filter is cause of unexpected wintertime filter clogging with biodiesel**
- **Confirm lack of fuel oxygen effect on GDI PM/PN emissions**
  - Test p-cymene blends – same vapor pressure and DBE as 4-methyl anisole – but no oxygen



- **Develop deeper understanding of fuel heat of vaporization versus RON effects on knock resistance for both ethanol and biomass oxygenates**
- **Continue outreach to biomass processors to obtain actual biomass-derived fuels for testing**

Summary

- **Research focused on barriers to petroleum displacement for conventional and advanced biofuels**
- **Properties of oxygenates present in partially upgraded biomass-pyrolysis oils were investigated.**
  - Generally high energy density and many high octane species are present
- **Single cylinder GDI engine studies of PM emissions found that PM/PN for gasoline-oxygenate blends follows the same trends as hydrocarbon fuels (correlates with PMI). Low vapor pressure oxygenates do not burn efficiently so produce less PM**
- **Knock limited spark advance for the biomass oxygenates was investigated and this work is ongoing**
- **DMF, a promising high octane oxygenate, was shown to decompose on standard gasoline stability tests – although antioxidant additives may prevent this**
- **Future work is directed at confirming conclusions about PM emissions and understanding the role of fuel heat of vaporization in knock resistance**

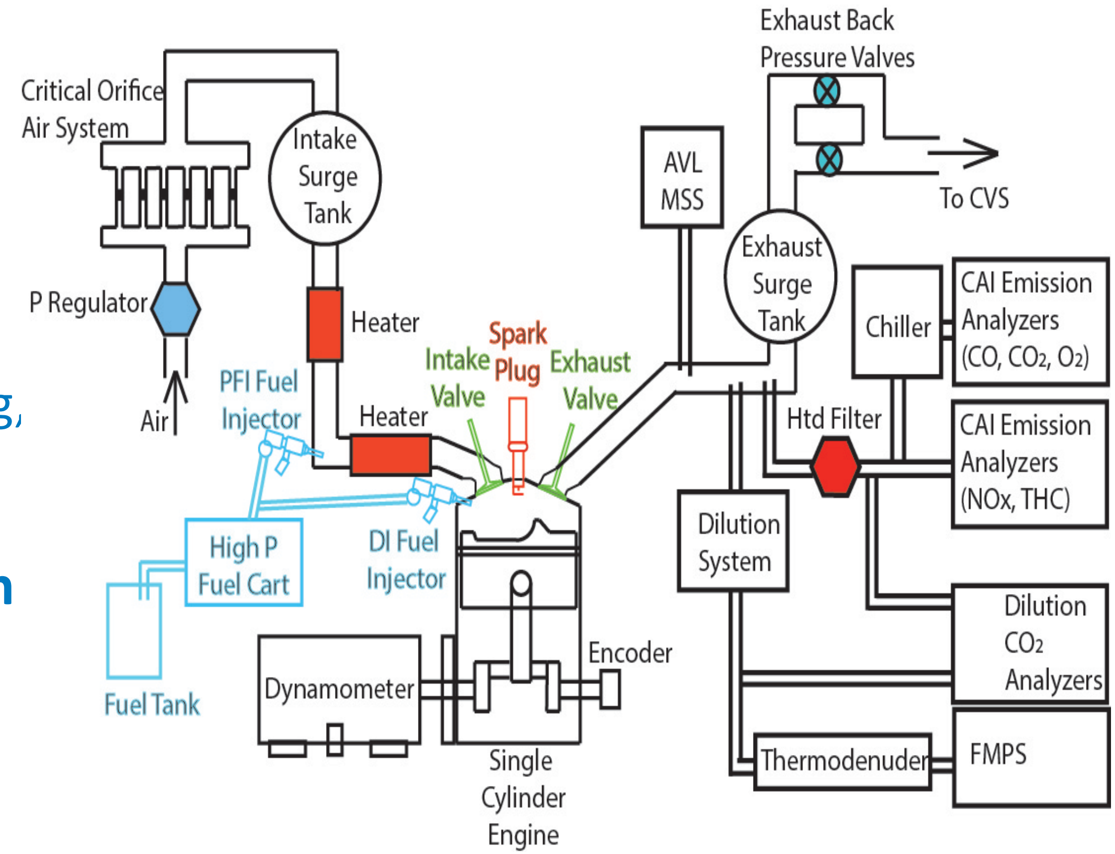
Technical Back-Up Slides

Approach/Strategy - Milestones

Month/ Year	Milestone or Go/No-Go Decision	Description	Status
12/2014	Milestone	Draft journal article on biomass oxygenate properties relevant to ASTM standards, infrastructure compatibility, behavior with water, and stability.	Complete (article published March 2015)
3/2015	Milestone	Draft journal article on gasoline boiling range oxygenates effects on particle emissions	Complete
6/2015	Milestone	Draft journal article on gasoline boiling range oxygenates effects on knock limit	On schedule
9/2015	Milestone	Draft journal article on diesel boiling range oxygenate effects on emissions and engine durability (with CSU)	On schedule

Single cylinder engine (SCE) setup

- **Wall-guided 0.5L DISI SCE**
- **Alternate upstream injector**
- **75-hp AC dynamometer**
- **Drivven engine controller**
  - Independent control of fuel injection timing, spark timing, fuel pressure, etc.
  - Combustion analysis
- **Critical flow orifice air system**
- **High-pressure fuel cart**
- **Emission measurement**
  - CAI raw regulated emissions bench
  - TSI Fast Mobility Particle Sizer (FMPS) w/ Dekati diluter & thermodenuder for PN
  - AVL Micro-soot sensor and dilution system for PM



SCE Schematic

Remaining Challenges and Barriers

- Barriers to commercialization of these fuels include economics of production and lack of data on performance. The current project aims to reduce both of these barriers through production cost reduction (reduced hydrotreating cost) and by providing knowledge on performance
- Obtaining actual pilot plant or small commercial plant fuel samples would be much more informative but has proven difficult given the lack of such production facilities for these fuels