NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Performance of Biofuels and Biofuel Blends




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Vehicle Technologies Program Merit Review – Fuels and Lubricants Technologies

May 15, 2012

Project ID: FT003

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline

Start date: Oct 2011

End date: Sept 2012

Percent complete: 66%

Program funded one year at a time

Budget

Total project funding

FY11: $1.1 M

FY12: $1.3 M – estimated

NBB cooperative research and development agreement provides around $500K to cost-share biodiesel research

Barriers

VTP MYPP Fuels & Lubricants Technologies Goals

- By 2013 identify light-duty (LD) non-petroleum based fuels that can achieve 10% petroleum displacement by 2025
- By 2015 identify heavy-duty (HD) non-petroleum based fuels that can achieve 15% petroleum displacement by 2030

Partners

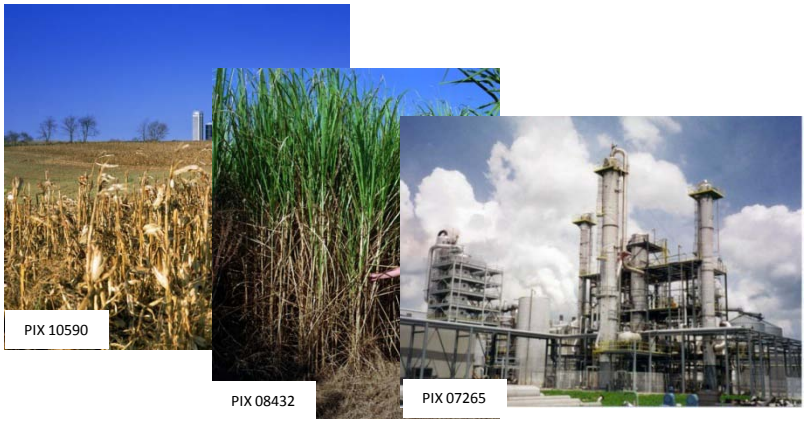
- National Biodiesel Board (NBB) and member companies
- Manufacturers of Emission Controls Association (MECA) and member companies
- Engine Manufacturers Association (EMA) and member companies
- Coordinating Research Council (CRC) and member companies
- Renewable Fuels Association
- Colorado School of Mines
- Colorado State University
- Oak Ridge National Laboratory
- State of Colorado
- Underwriters Laboratories
- Many biofuels startups

Relevance

Objective: Solve technical problems that are preventing expanded markets for current and future biofuels and biofuel blends

Necessary to achieve MYPP petroleum displacement goals and renewable fuel standards requirements

Research at the interface of fuel production and engines and infrastructure



Approach

- **Broad scope of biofuels: ethanol to biodiesel to next-generation oxygenate and hydrocarbons**
- **Quality and performance properties, compatibility with engines, lubricants, and emission controls; and impacts on emissions**

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

✓Industry collaborations guide our work to be relevant
✓Collaborations with other labs and universities broaden our effective capability

Milestones

Date	Milestone or Go/No-Go Decision	Status
Mar-11	**Ethanol Blender Pump Fuel Quality Survey.** Fifteen blender pump stations were sampled in July 2010. Conventional gasoline, flex fuel vehicle (FFV) fuel, and the two lowest blends were collected. Fuel properties were compared to the ASTM D4814 and D5798 specifications.	Complete
Apr-11	**Properties of gasoline/oxygenate blends.** Experimental study assessing the properties of individual C2-C5 alcohols plus several cellulose-derived oxygenates blended into summer, winter, and shoulder-season blendstocks for oxygenate blending.	Complete
May-11	**Impact of pre-oxidation on the stability of B100.** Experiments assessing the actual stability of poor stability B100 that is brought into spec by blending with antioxidant or stable B100	Complete
Aug-11	**Impact of biodiesel ash forming constituents on selective catalytic reduction (SCR) catalyst performance.** Effects of Na and K on both LD and HD configurations are being measured in accelerated tests.	Complete
Jul-12	**Non-methane organic gas emission effects of gasoline oxygenate blends.**	Likely to be postponed

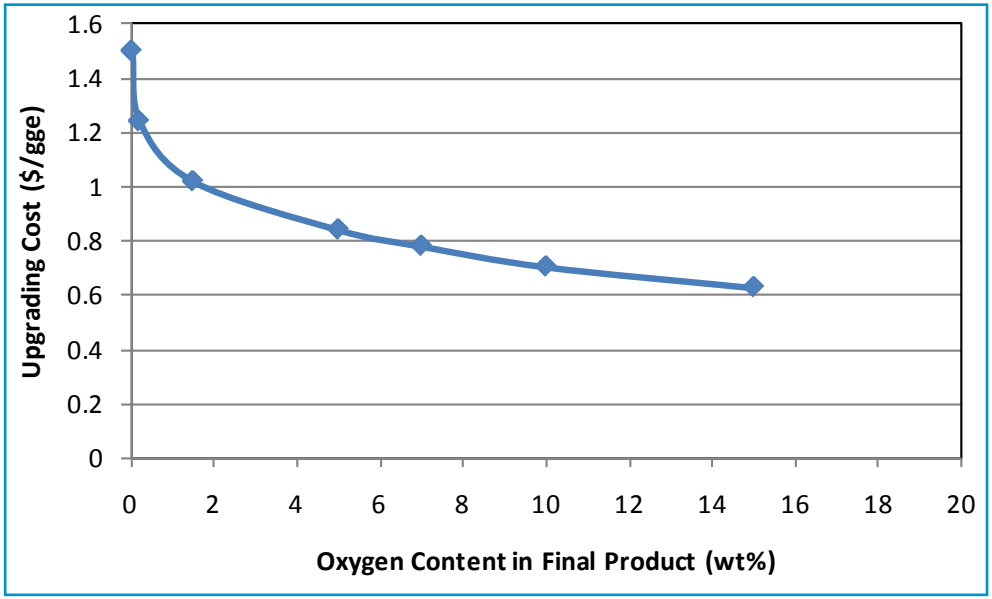
List of Technical Accomplishments

1. **Assessment of Acidic Components in Hydrotreated Biomass Pyrolysis Oil**
2. **Chemistry and Properties of Mixed Alcohols Produced From Biomass-Derived Syngas**
3. **Performance Properties of Hydrocarbon Renewable Diesel Fuels**
4. **B20 Diesel Oxidation Catalyst (DOC)/Diesel Particulate Filter (DPF)/SCR Durability Research**
5. **Effect of Biodiesel on Emissions from Transit Buses Spanning the 1998-2010 Emission Regulations**
6. **Impact of Pre-Oxidation on Stability of B100**
7. **Saturated Monoglyceride Effects on Biodiesel Low-Temperature Performance**
8. **E85 Quality Survey and ASTM Specification Changes**
9. **2011 Wintertime B100 Quality Survey**
10. **New Laser-Desorption Ionization Time-of-Flight Mass Spec Approach to Analysis of Oxygenates in Biomass Pyrolysis Oils**
11. **Biodiesel Lube Oil Dilution in both LD and HD Systems with Active Regeneration**
12. FFV Emission on Blender Pump or Co-mingled Fuels (E40)
13. Development of Dispenser Retrofit Kits for E15
14. Improved Analysis Methods for Glycerides in Biodiesel

Presented Today

See Technical Backup Slides

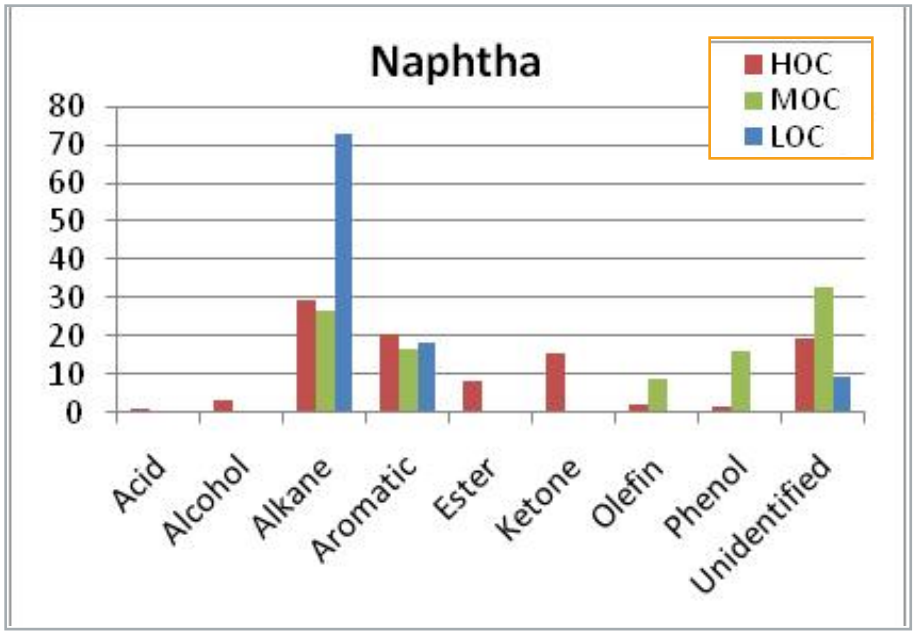
Can Oxygenate Be Tolerated in Drop-in Fuel?



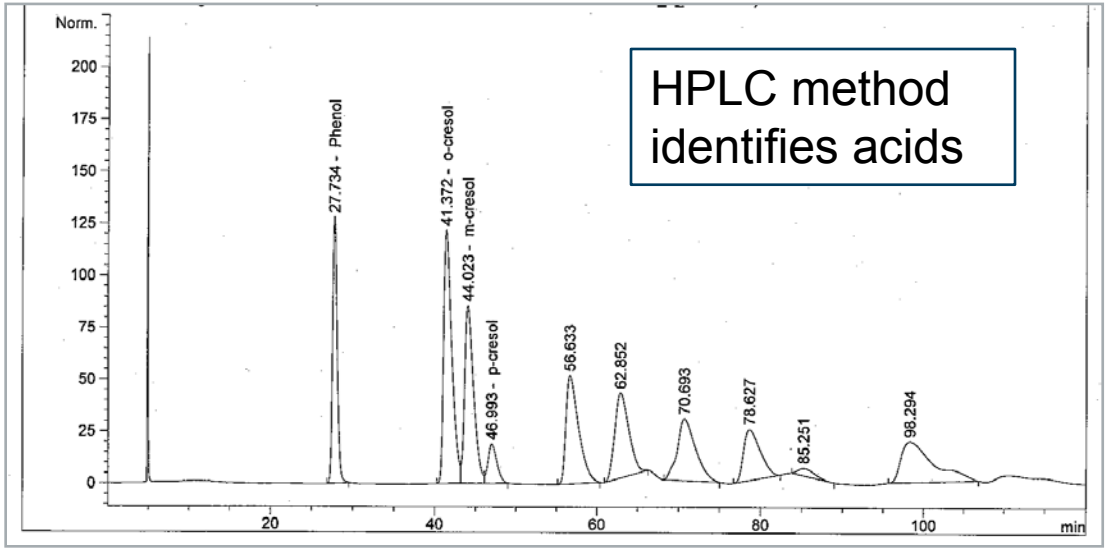
Economic evaluation of biomass pyrolysis oil upgrading costs as a function of final product oxygen content
Arbogast, S.V. *Upgrading Requirements for the Transport and Processing of Pyrolysis Oil in Conventional Petroleum Refineries*, Houston, TX: Global Energy Management Institute, 2009.

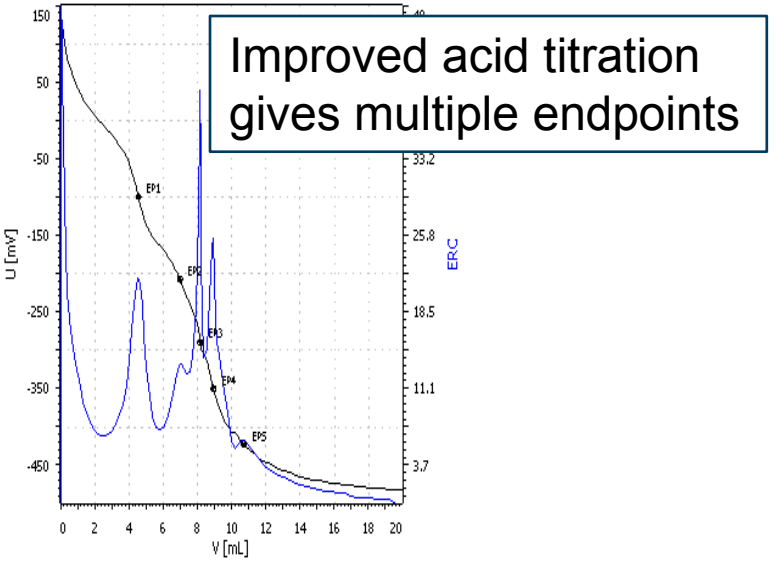
- **Article of faith that "drop-in" fuels are hydrocarbon**
- **But biomass has a high oxygen content**
- **Economically rejecting this oxygen may not be possible**
- **Many conversion processes produce oxygenates**
  - Biochemical to sugar/fermentation
  - Thermochemical mixed alcohol
  - Acid hydrolysis
  - Lignin depolymerization
  - Fast pyrolysis

Technical Accomplishment: Characterization of Acids in Hydrotreated Pyrolysis Products



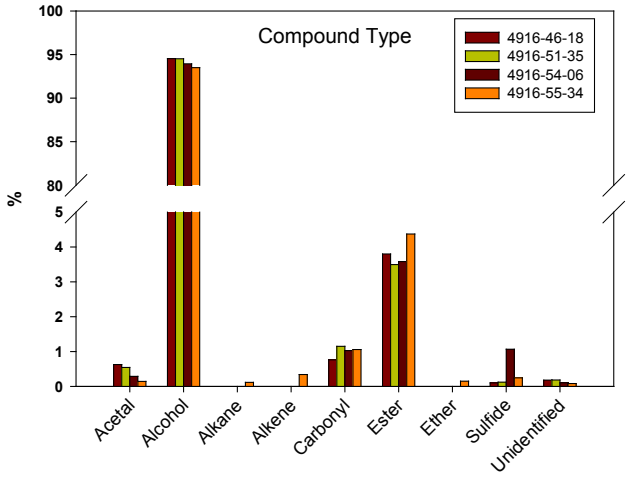
- Pyrolysis oil hydrotreated to different levels of oxygen content and distilled
- Developed improved approach to acid characterization
- Differentiate weak and strong acids
- Ongoing work to improve HPLC method (move to UPLC)
- Evaluating performance of materials with residual oxygen

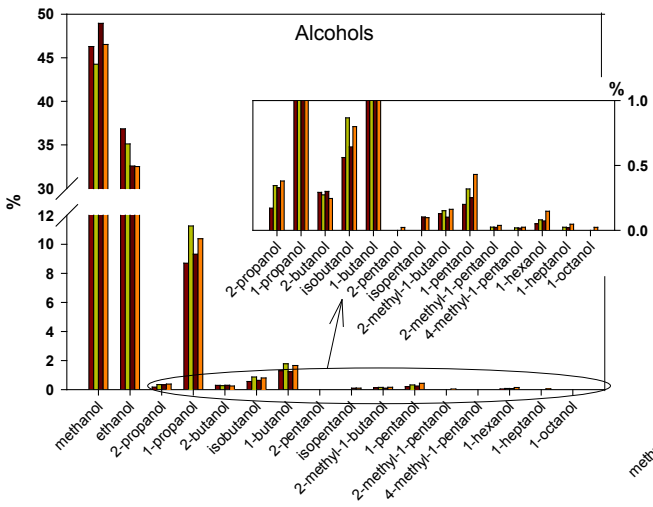


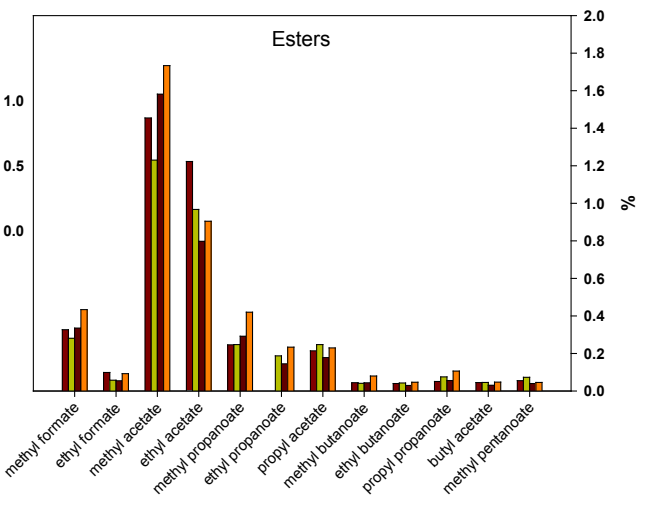


Technical Accomplishment: Mixed Alcohols from Biomass-Derived Syngas

- Properties and composition of mixed alcohols
  - Effect of alcohol composition on gasoline properties
  - Impurities and relevance to gasoline performance
  - Advanced distillation (with NIST) and fate of impurities
  - Emission testing (if adequate funding – fabricated blends)
- Properties of gasoline blends
  - Benefits of ethanol with long-chain alcohols (for Reid vapor pressure)
  - Gasoline under Octamix waiver can contain 5% max methanol plus 2.5% minimum C2-C8 alcohols – is this more economical?

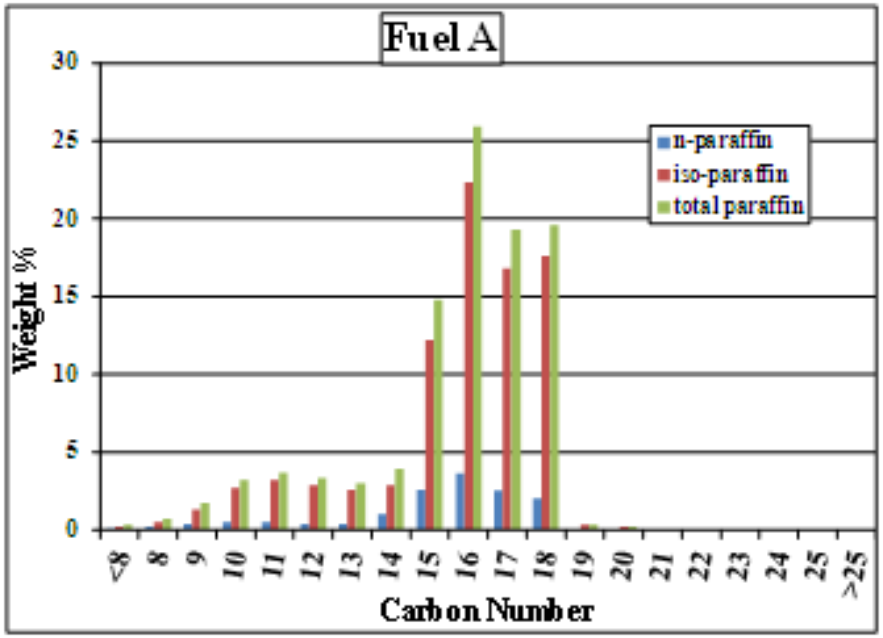


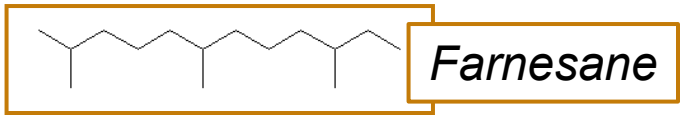


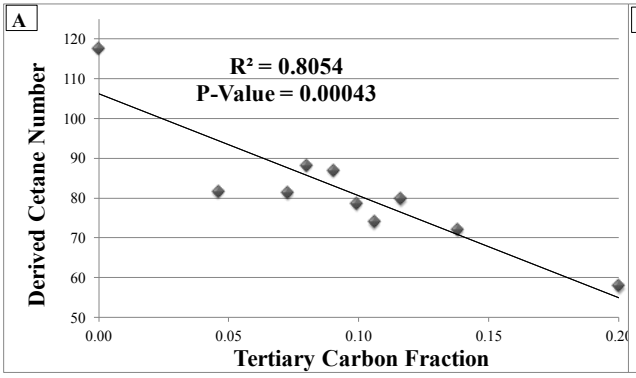


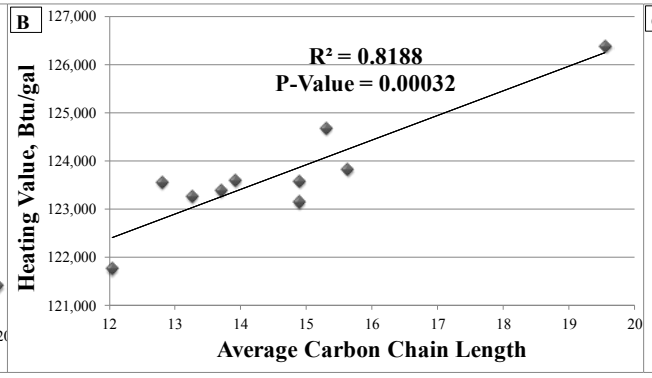
Technical Accomplishment: Performance Properties of Hydrocarbon Renewable Diesel Fuels

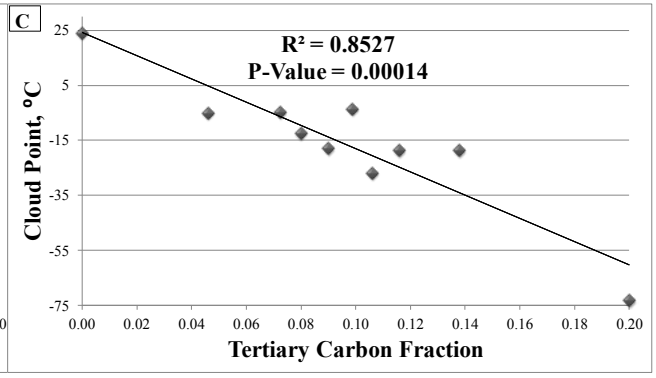
- Commercial and prototype hydrocarbon diesel fuels
  - 10 samples from industry partners
  - Produced by hydroisomerization and fermentation
- High quality, high cetane number materials
  - Low level of residual oxygen in some samples
- Fat/veg oil derived fuels are highly isomerized (80%+)











Technical Accomplishment: Biodiesel Catalyst Durability Study


Photo: Aaron Williams, NREL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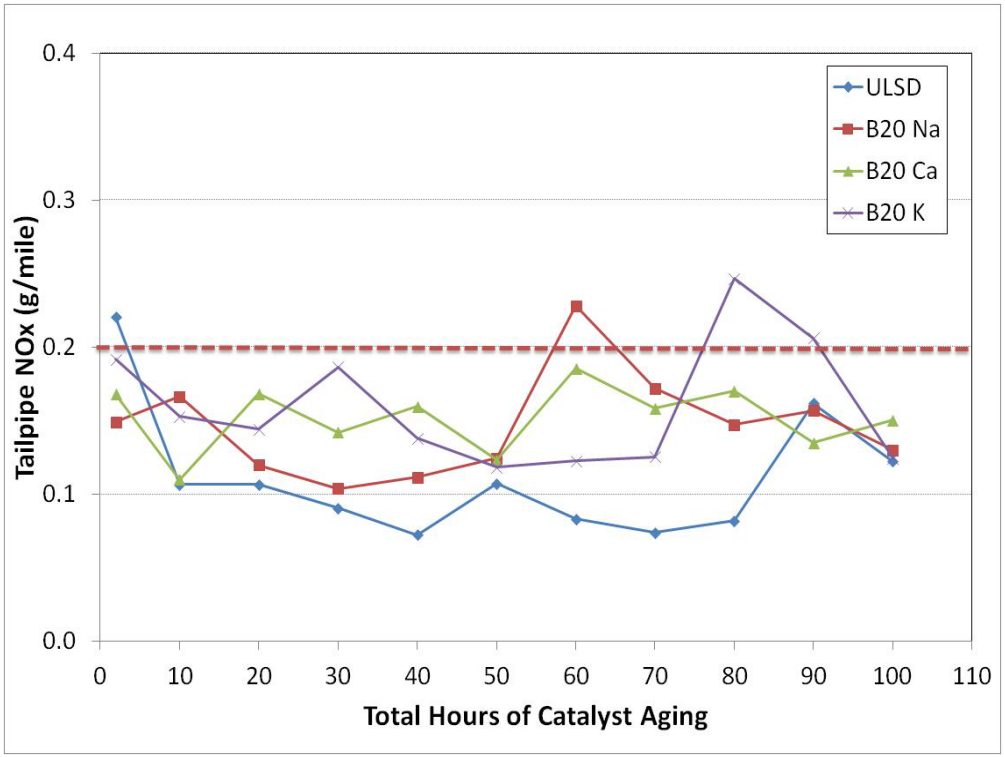
Used catalysts being characterized by ORNL and Ford

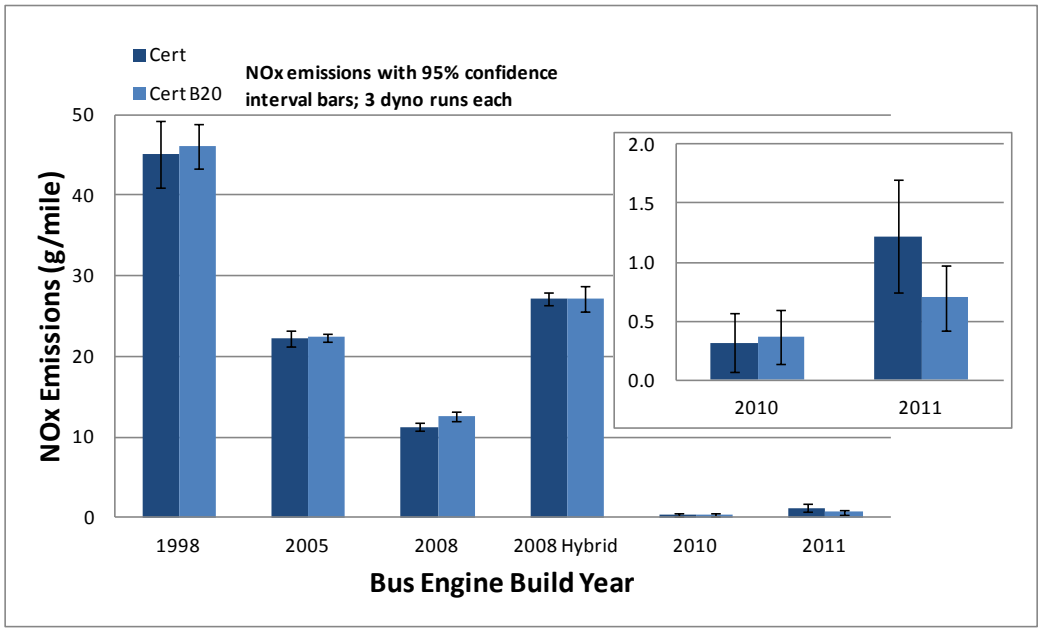
- Accelerated aging of LD diesel catalysts
- 2011 Ford F250 with DOC+SCR+DPF
- Ultralow sulfur diesel, B20+Na, B20+K and B20+Ca
- After 150,000 miles equivalent exposure, no significant emission degradation was observed
- Biodiesel metals at current spec limit appear to have no negative effect on LD catalyst durability

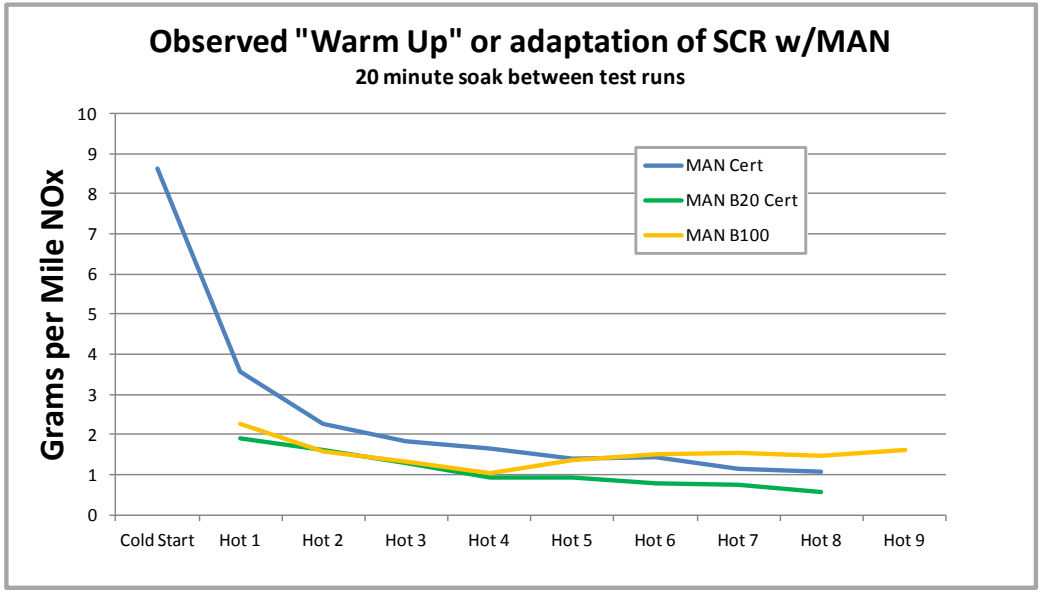


Technical Accomplishment: B20 Bus NOx Comparison

- 6 buses tested on NREL's Renewable Fuels and Lubricants (ReFUEL) laboratory HD Chassis Dynamometer
- B20 effect on NOx statistically significant in fewer than half of comparisons
- Note near-zero NOx for 2010-2011 buses with SCR
  - *Eliminates B20 and B100 effect on NOx emissions*

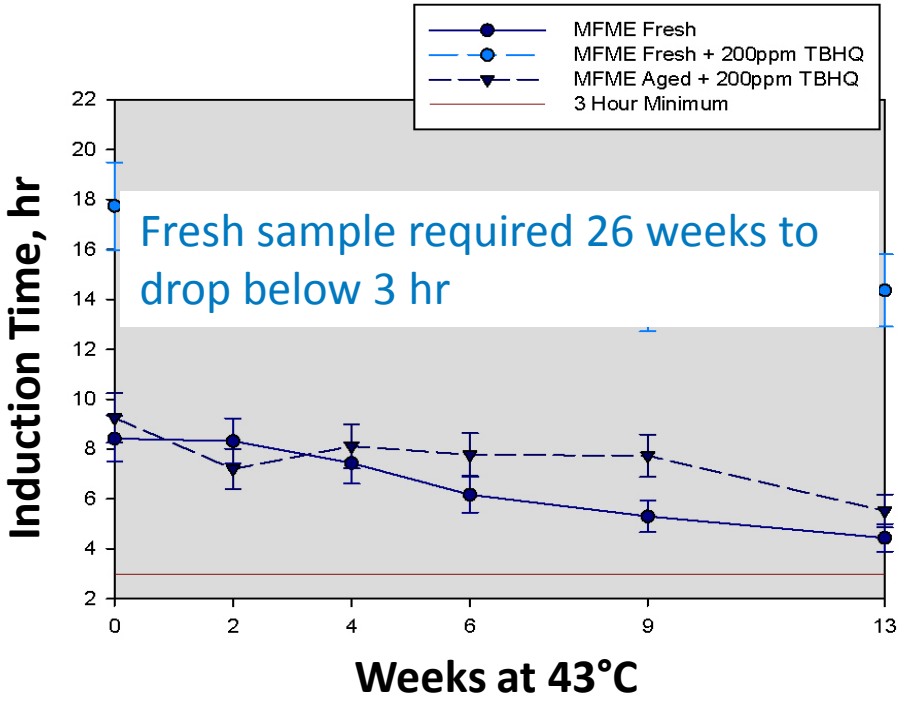
Photo: Mike Lammert, NREL

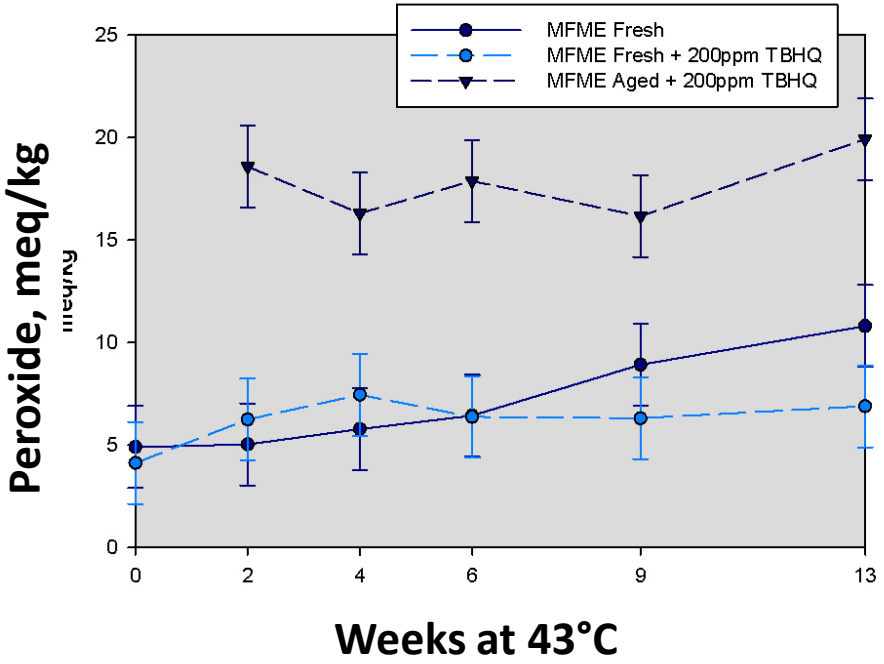




Technical Accomplishment: Impact of Pre-Oxidation on B100 Stability

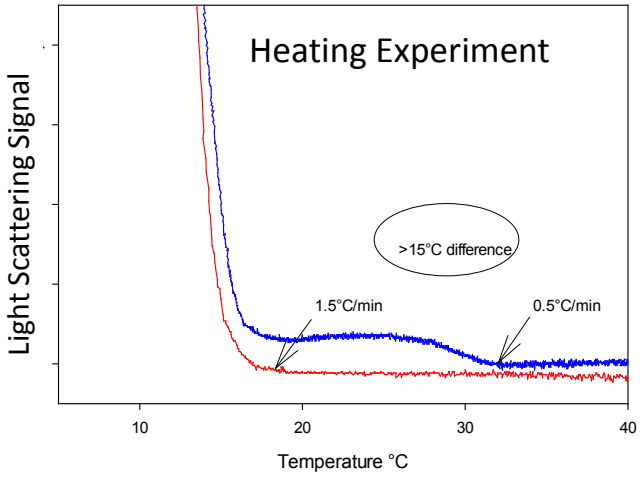
- **Demonstrated that biodiesel oxidized to fail specification can be rescued:**
  - Brought back in to spec by addition of antioxidants and will oxidize at the same rate as it did initially
  - Higher peroxide in pre-oxidized material expected to dominate and cause rapid oxidation
  - Indicates that biodiesel fatty acid methyl esters makeup and antioxidant content are the primary factors, not degree of oxidation
- **Fundamentally changes expectations regarding biodiesel oxidation and the potential to store for long time periods (3 years+)**

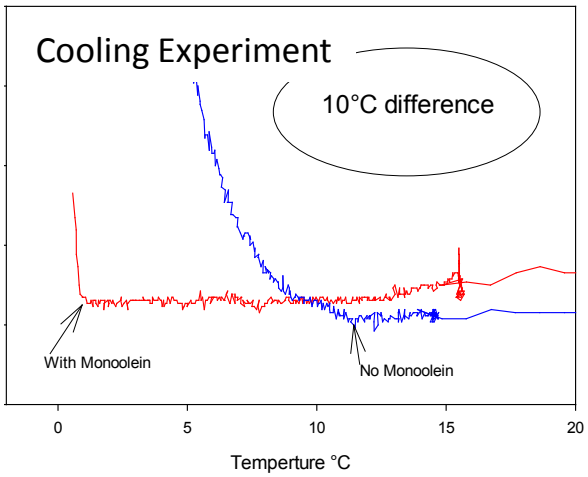


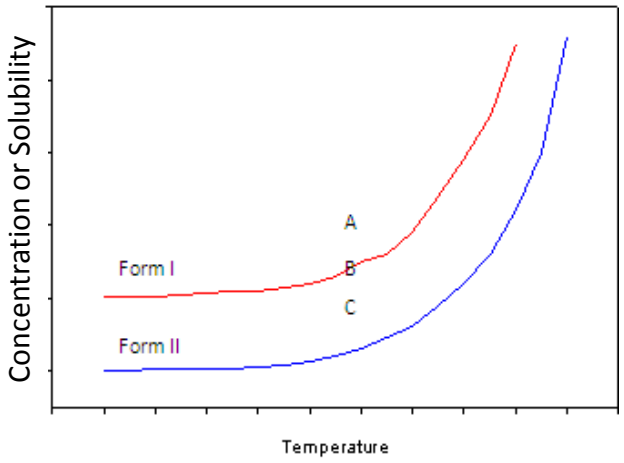


Technical Accomplishment: Saturated Monoglyceride (SMG) Effects on Biodiesel Low-Temperature Performance

- **Prior study showed that SMG precipitate as a metastable form that transforms into a much less soluble, stable form**
- **Likely primary cause of unexpected cold weather problems for biodiesel**
- **Recent work has demonstrated a number of features of this phenomenon**
  - It can occur for any biodiesel feedstock
  - Laboratory heating/cooling rates frequently are too fast
  - Other minor impurities can affect phase conversion
  - Main cause of biodiesel failing cold soak filtration test
  - It is a solvent-mediated polymorphic phase transformation (100 years of scientific literature)







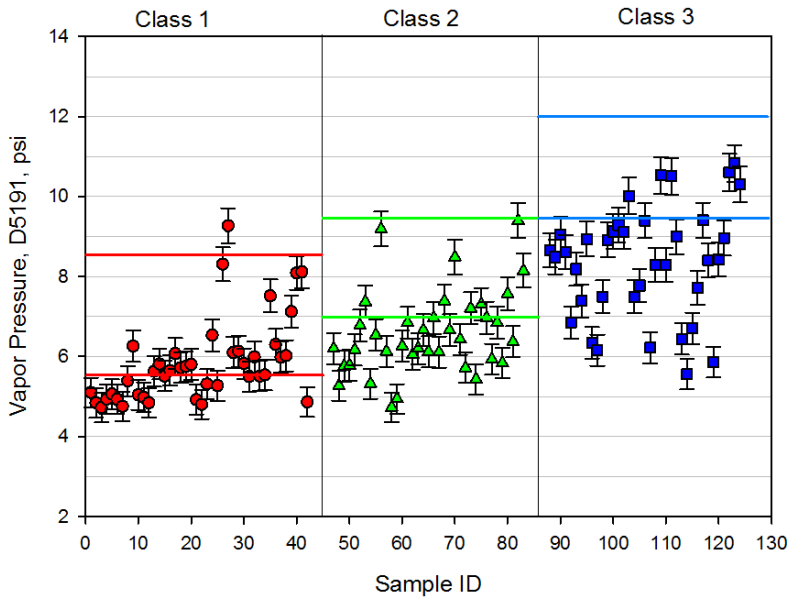
Technical Accomplishment: E85 Survey and Specification Changes

- **NREL worked with CRC to assess the quality of E85 nationwide**
- **Vapor pressure requirements for gasoline and E85 are critical for cold starting and driveability**
- **Prior survey showed high failure rate for E85, and there were many anecdotal reports of difficulty starting and poor performance**
- **Changes were made to the D5798 ASTM specification to allow higher levels of gasoline to increase vapor pressure**
- **New survey showed that FFV drivers will see improved performance – may lead to higher usage of E85**

- Survey of 106 samples from around U.S.
- All three volatility classes
- Nearly 50% of samples met vapor pressure requirements
- A marked improvement over previous surveys

National 2010-2011 Survey of E85: CRC Project E-85-2

http://www.nrel.gov/docs/fy12osti/52905.pdf

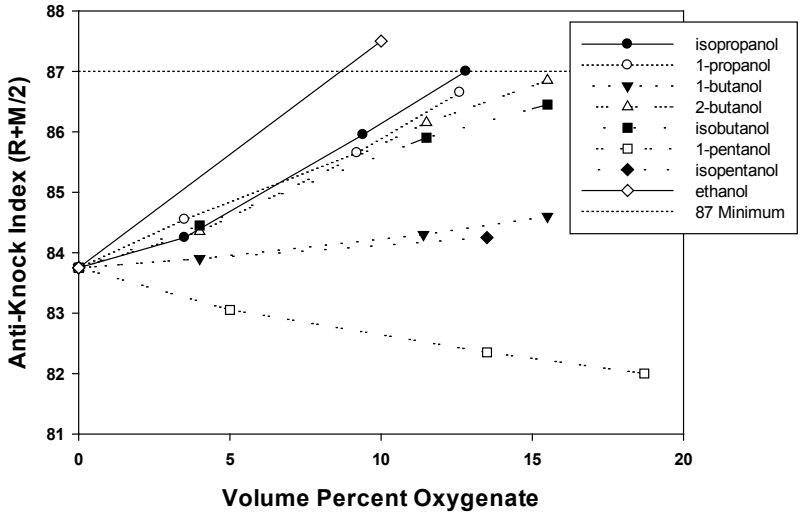


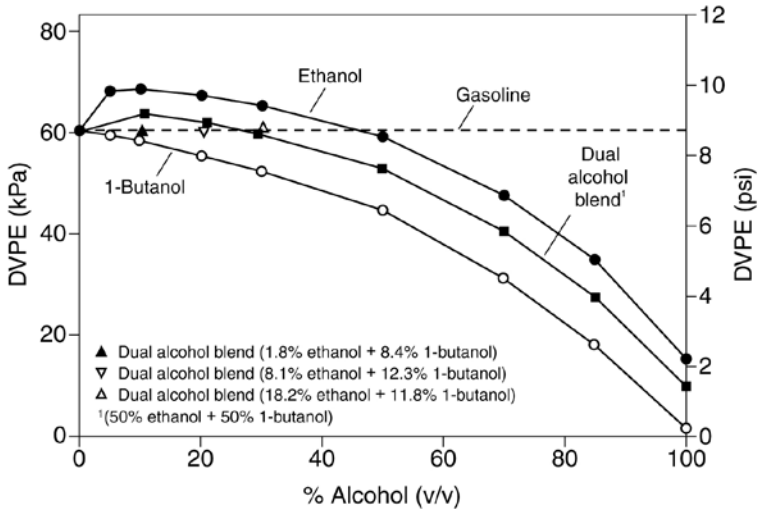
Collaboration and Coordination with Other Institutions

- **Assessment of Acidic Components in Hydrotreated Biomass Pyrolysis Oil**
  - National Bioenergy Center (NREL)
  - National Advanced Biofuels Consortium (NREL)
  - Pacific Northwest National Laboratory
  - Valero Energy Corporation
- **Performance Properties of Hydrocarbon Renewable Diesel Fuels**
  - Chevron Global Downstream Technology
  - Innospec Fuel Specialties
  - Lubrizol Corporation
  - Dynamic Fuels
  - Neste Oil Corporation
  - Biofuels startup companies wishing to be anonymous
- **B20 DOC/DPF/SCR Durability Research**
  - MECA and member companies, including
    - Umicore
    - BASF Catalysts, LLC
  - Caterpillar
  - Ford Motor Company
  - NBB (cofunding)
  - EMA and member companies
  - Oak Ridge National Laboratory
- **Biodiesel Transit Bus Emissions**
  - Transit agencies in Denver, Ft. Collins, Aspen, and Colorado Springs, CO
  - DOE Clean Cities Program (cofunding)
- **Impact of Pre-Oxidation on Stability of B100**
  - Renewable Energy Group
  - ADM
  - Griffin Industries
- **Saturated Monoglyceride Effects on Biodiesel Low-Temperature Performance**
  - Phase Technology, Inc.
  - Innospec Fuel Specialties
- **E85 Quality Survey and Specification Changes**
  - CRC (cofunding)
- **2011 Wintertime B100 Quality Survey**
  - NBB and member companies
  - DOE Clean Cities Program (cofunding)
- **Others**
  - Renewable Fuels Association
  - Colorado School of Mines
  - Montana State University
  - Flint Hills Resources
  - BP
  - USDA: Agricultural Research Service

Proposed Future Work – Partial List

- **Acid in ungraded pyrolysis oils and distillate fractions**
  - UPLC for detailed speciation of acids present
  - Improved titration for pKa measurement
- **Effect of mixed alcohols on gasoline properties and emissions**
  - Ethanol-butanol-gasoline blends
  - Syngas-derived mixed alcohols
  - Emissions with emphasis on quantification of carbonyls
- **ASTM specifications**
  - Specification development for butanol blendstock
  - Inclusion of E15 in gasoline
  - Improved analysis of glycerides in biodiesel
- **Definition of Drop-In Fuels**
  - Effect of specific oxygenates on gas/diesel properties, storage and handling
  - Compatibility with materials
- **Impact of High Octane Biofuels on Di Engine Efficiency**
  - Effects of RON, MON, heat of vaporization, and compression ratio





Summary

- **Guidance from last year's AMR has improved the quality of this activity**
- **In particular, the emphasis is shifting to a focus on defining what is a drop-in fuel**
- **Studies focused on impurities in biofuels and how these are measured and affect performance:**
  - Acids in hydrotreated biomass pyrolysis oils
  - Monoglycerides and metals in biodiesel
- **Studies also examined the performance of new fuels in storage and handling, as well as engine operation**
- **Fuel quality surveys led to improved ASTM specifications**

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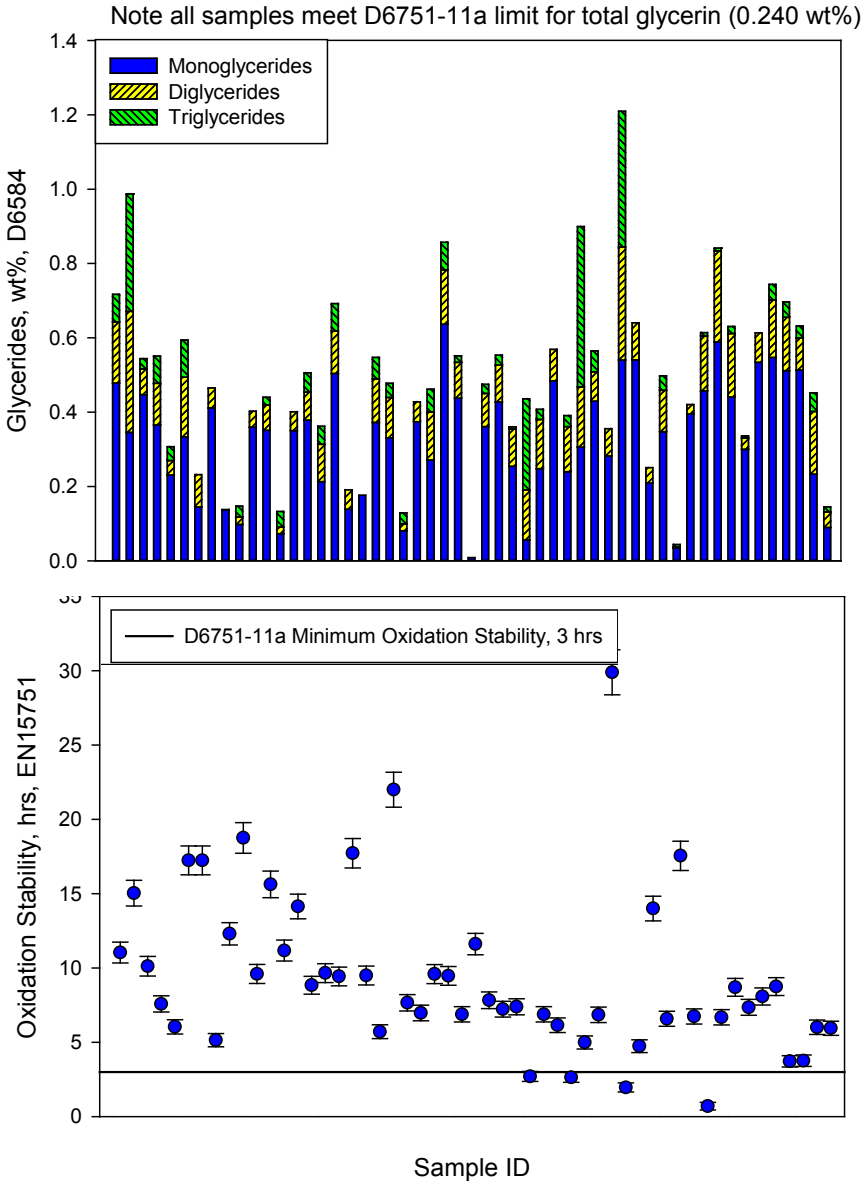
Technical Back-Up Slides

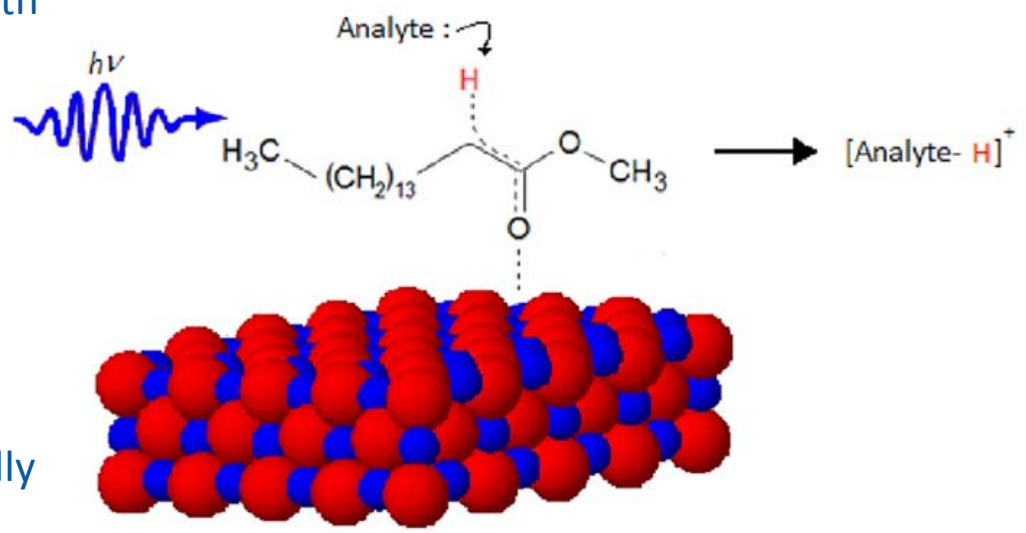
Technical Accomplishment: 2011 Wintertime B100 Survey

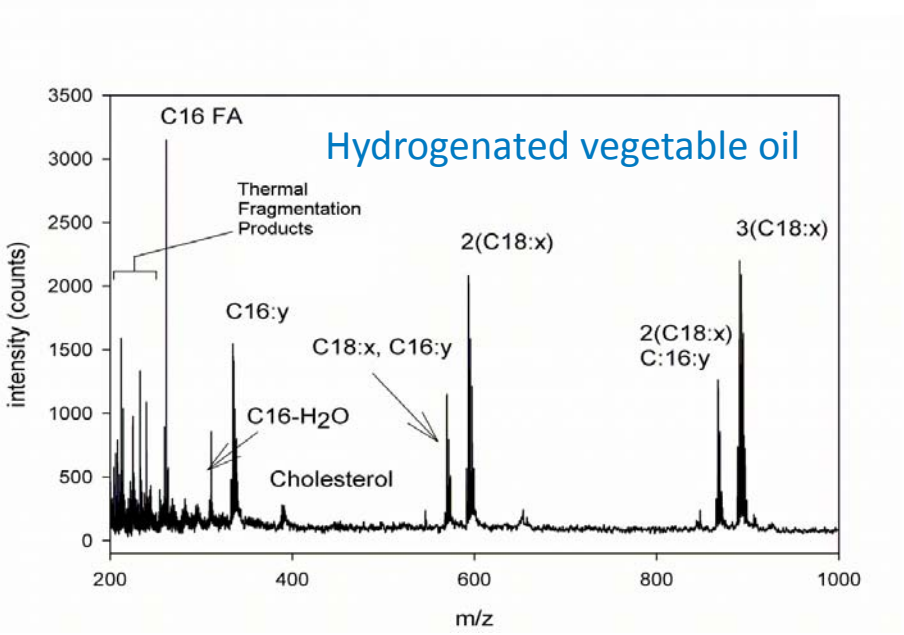
- **Completion of B100 producer quality survey (samples obtained from 53 producers)**
- **2011 had highest ever production volume of B100 in the US: 1.1 billion gallons**
- **B100 almost always meets the quality specifications, a marked improvement over previous surveys**
  - 4% failure on oxidation stability
  - Less than 2% failure on cold soak filterability, metals, and flashpoint
  - No failures on glycerin or acid value

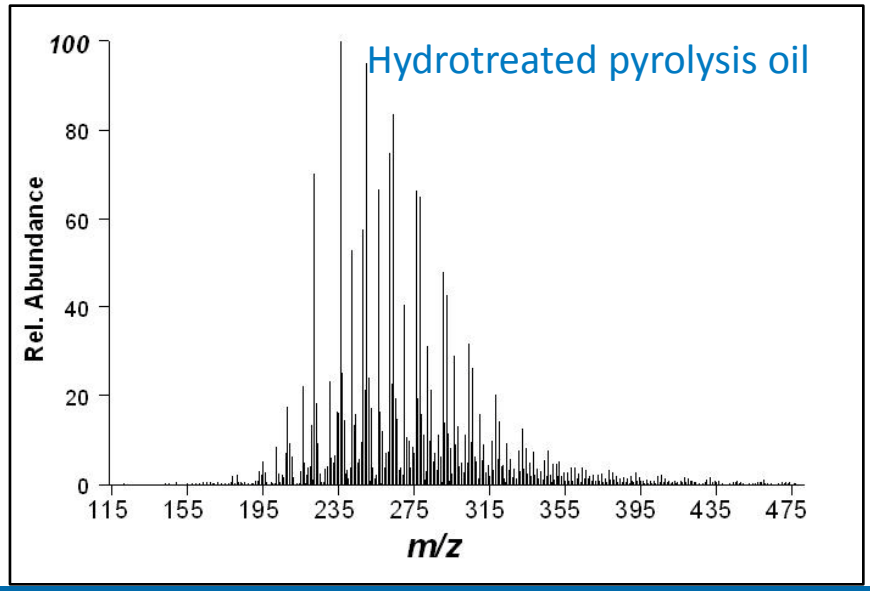


Metal Oxide Laser Ionization Mass Spectrometry (MOLI MS) :

- Interaction of oxygen containing analytes with surface ions from metal oxide nanoparticles results in charge transfer and ionization between two neighboring analytes when irradiated with an ultraviolet laser.
- Surface doping with a small ester allows ionization of almost any analyte with free electrons.
- System ideal for complex samples not typically amenable to separation-based analyses.







B20 Impact on Lube Oil Dilution

- **Study shows increased lube oil dilution for LD diesel running on B20**
  - 4,000-mile result. Lube oil drain interval is 10,000 miles
- **Diesel fuel levels appear to stabilize at about 4% in oil**
- **Biodiesel has a higher boiling point and continues to increase**
  - Biodiesel in oil could exceed 5% at oil drain
- **It is unclear if lubricants can handle 5% biodiesel content – or not**
- **Additional study required to understand if this is a limiting issue**
- **Note that in prior testing with MD/HD engine we did not observe increased lube oil dilution for B20**