Performance of Biofuels and Biofuel Blends

Robert McCormick

Vehicle Technologies Program Merit Review – Fuels and Lubricants Technologies

May 16, 2013

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

Timeline
Start date:  Oct 2012
End date:  Sept 2013
Percent complete:  66%

Program funded one year at a time

Budget
Total project funding
FY12:  $1.3 M
FY13:  $0.77 M – to date

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 State University
• Oak Ridge National Laboratory
• State of Colorado
• Underwriters Laboratories
• Many biofuels startups
## Milestones

<table>
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<tr>
<th>Date</th>
<th>Milestone or Go/No-Go Decision</th>
<th>Status</th>
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<tr>
<td>Nov-12</td>
<td><strong>Non-methane organic gas emission effects of gasoline oxygenate blends.</strong></td>
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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/Strategy

• Performing research on the broad scope of biofuels: ethanol to biodiesel to next-generation oxygenate and hydrocarbons

• Quality and performance properties, compatibility with infrastructure, engines, lubricants, and emission controls; and impacts on emissions

✓ Industry collaborations guide our work to be relevant
✓ Collaborations with other labs broaden our effective capability (industry, national labs, universities)
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)

• But biomass has a high oxygen content and many conversion processes produce oxygenates

• Can economics be improved if not all of this oxygen is removed?

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

- Biomass has high oxygen content:
  - 40 to 60 wt%
  - Molar O/C about 0.6
- Economically rejecting this oxygen may not be possible

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

Economic evaluation of biomass pyrolysis oil upgrading costs as a function of final product oxygen content
**Technical Accomplishment:** Characterization of Acids in Hydrotreated Pyrolysis Products

- Developed improved approach to acid characterization - multiple endpoints not detected by standard Total Acid Number measurement (ASTM D664)
- Differentiate weak (phenolic) and strong (carboxylic) acids based on pH buffer calibration
- Low detection limits observed for model compounds in heptane and diesel fuels
- In a bio-oil matrix, titration of phenol showed poor detection limit, indicating interference in titration. Further refinement underway

**Standards in Heptane**

**Phenol not detected by titration at TAN<6**

**Hydrotreated Bio-oil Matrix**

**Sample Weight (g)**

- Solid = actual value
- Dotted = measured
Technical Accomplishment: Biomass Residual Oxygenate Effects on Diesel Performance Properties

Residual Oxygenates Tested in Diesel

- Blended into certification diesel at 2 vol%
- Assessed by ASTM D975 standard plus oxidative (D2274) and thermal (D6468) stability
- Results:
  - Carbon residue – no change
  - Cloud point – no change
  - Copper corrosion – no change
  - Conductivity – no change
  - Lubricity – improved (548 μm wear scar base fuel)
  - Oxidation stability – improved (7.9 mg/100 ml base fuel)
  - Thermal stability – no change
- Water solubility of phenols may limit their concentrations in a drop-in fuel:
  - Phenol – about 8 wt%
  - Cresols – about 3 wt%
  - Xylenols – about 0.5 wt%

Materials compatibility and engine tests ongoing
Properties and Emissions of Gasoline/Ethanol/Butanol Blends

- Properties and emissions for gasoline blended with ethanol, 1-, 2-, and iso-butanol, and mixtures of ethanol and butanol were measured.
- At constant 5.5 wt% oxygen, blends of 12% i-butanol/7% ethanol showed no increase in vapor pressure.
- Ethanol was more effective than the other alcohols at reducing CO emissions (for this vehicle).
- Ethanol produced much higher unburned alcohol emissions, but much lower carbonyl emissions, than the butanols – such that NMOG was largely unaffected.
- 12% i-butanol/7% ethanol blend significantly reduced NMOG relative to cert gasoline because both carbonyl and unburned alcohol emissions were lower.

Technical Accomplishment: 2009 Honda Odyssey LA-92 Cycle

- Major carbonyl emissions:
  - Ethanol: formaldehyde, acetaldehyde
  - 1-butanol: formaldehyde, acetaldehyde, butyraldehyde
  - i-butanol: formaldehyde, acetone, methacrolein

NATIONAL RENEWABLE ENERGY LABORATORY
Lipid Biomass

• Natural fats and oils (including algal oil)

• Terpenoid natural products (aka Isoprenoid)
  – Pine turpentine
  – Fermentation

• Less than 10% oxygen content
  – Removed by hydroisomerization (fats and oils) or hydrogenation (terpenoid)

Terpenoids:
- Monoterpenes
- Sesquiterpenes

Fats and Oils:
Technical Accomplishment: Properties of Terpene Biofuels

- A range of terpene compounds characterized
- All unsaturated or oxygenated

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<th>Property</th>
<th>Method</th>
<th>P-cymene</th>
<th>β-pinene</th>
<th>1,4-cineole</th>
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Technical Accomplishment: Properties of Terpene Biofuels

- Hydrogenation may improve properties
- Ring opening hydrogenation collapses all monoterpenes to 2,6 dimethyl octane or similar compounds
- Bicyclic alkanes are dense and may have high smoke point

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Biodiesel

- Fatty acid methyl esters – a low cost approach to fuels from fats and oils
- 1.1 billion gallon in United States (in both 2011 and 2012)
- Produced from soy oil, animal fats, waste cooking oil, corn oil from corn ethanol plants,…
- Many new feedstocks emerging: canola, camelina, tall oil fatty acids, algae,…
Technical Accomplishment: Long-Term Storage of Biodiesel Blends

- Simulating 3 years storage of B5 and B20 blends (D4625 accelerated storage)
  - 2 year simulation completed (26 weeks storage)
  - Measuring Rancimat induction time (6 hr minimum)
- Saturated vs unsaturated biodiesel, different antioxidant levels, hydrocracked and hydrotreated diesel fuels
- B5 blends all meet 6 hr requirement (at 2 years)
  - Higher oxidation rate for more unsaturated biodiesel, lower antioxidant (lower initial B100 Rancimat)
  - Blends with hydrocracked diesel showed significantly lower stability
- B20 blends meet 6 hr minimum if initial B100 Rancimat is 6 hr
  - Blends with low polyunsaturate B100 also met requirement for 3 hr initial B100 Rancimat
  - Effect of diesel fuel chemistry not evident in B20 data
Technical Accomplishment:

Saturated Monoglyceride (SMG) Effects on Biodiesel Blend Low-Temperature Performance

- Common impurity in biodiesel, present at up to about 0.5 wt%
- Likely responsible for most incidents of “unexplained” cold weather filter clogging
- Completed a factorial designed study (over 140 samples) to examine effects of several variables on Cloud Point (CP):
  - SMG
  - Saturated FAME
  - Diesel CP
  - Diesel aromatic content
- SMG had the largest effect on CP
- Increasing biodiesel blend level at constant SMG content reduced CP
  - Solubility effect
- Increasing saturated FAME content had no effect at B5 or B10, but increased CP at B20
- Higher diesel aromatics reduced the CP effect of both SMG and saturated FAME
  - Solubility effect
# 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

## Biomass Residual Oxygenate Effects on Diesel Performance
- Colorado State University
- Underwriters Laboratories

## B20 DPF/DOC/SCR Durability Research
- MECA and member companies, including
  - Umicore
  - BASF Catalysts, LLC
- Caterpillar
- Ford Motor Company
- National Biodiesel Board
- EMA and member companies
- Cummins
- Oak Ridge National Laboratory

## Ethanol/Butanol Blend Performance
- SGS-Environmental Testing Corporation

## FFV Emissions/Adaption on E40
- Colorado Department of Public Health and Environment

## Terpene Biofuels Characterization
- J Craig Venter Institute

## Biodiesel Transit Bus Emissions
- Transit agencies in Denver, Ft. Collins, Aspen, and Colorado Springs, CO
- DOE Clean Cities Program (cofunding)

## Long-Term Stability of Biodiesel Blends
- Renewable Energy Group
- ADM
- Griffin Industries
- Flint Hills Resources
- National Biodiesel Board

## Saturated Monoglyceride Effects on Biodiesel Low-Temperature Performance
- Phase Technology, Inc.
- Innospec Fuel Specialties
- Flint Hills Resources

## Others
- Renewable Fuels Association
- USDA: Agricultural Research Service
Proposed Future Work

• Definition of Drop-In Fuels
  • Effect of specific oxygenates on gas/diesel properties, storage and handling
  • Compatibility with materials
  • Engine operation and emissions
  • Expansion to employ actual biomass products rather than model compounds

• Acid in upgraded pyrolysis oils and distillate fractions
  • UPLC for detailed speciation of acids present
  • Improved titration for pKa measurement
  • Measurement of corrosion

• ASTM specifications
  • Specification development for butanol blendstock
  • Inclusion of E15 in gasoline standard
  • Variables affecting ethanol conductivity and correlation to corrosivity

• Impact of High Octane Biofuels on DI Engine Efficiency
  • Effects of RON, MON, heat of vaporization, and compression ratio
  • Distillation curve and heat of vaporization as a function of fraction evaporated

• IQT Study of Lubricant Effects on Low-Speed Pre-Ignition in Highly Boosted Engines

• Completion of 3 year Biodiesel Blend Storage Study
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
Technical Back-Up Slides
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*
• Potential for very high NOx emissions on cold start and for low-speed/low-load operation

Observed "Warm Up" or adaptation of SCR w/MAN
20 minute soak between test runs

NOx emissions with 95% confidence interval bars; 3 dyno runs each

Bus Engine Build Year

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<td>Cert</td>
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Grams per Mile NOx

Cold Start Hot 1 Hot 2 Hot 3 Hot 4 Hot 5 Hot 6 Hot 7 Hot 8 Hot 9

Photo: Mike Lammert, NREL
Fuel Surveys and Their Influence on ASTM Specifications

- Vapor pressure requirements for gasoline and E85 are critical for cold starting and driveability
  - Many anecdotal reports of difficulty starting and poor performance
- Survey conducted in 2009 showed as many as 90% of samples failing minimum RVP
- Changes were made to the D5798 ASTM specification to allow higher levels of ethanol to increase vapor pressure
- NREL worked with CRC to assess the quality of E85 nationwide in and published report
  - Conducted in late 2010 and early 2011
- New survey shows large increase in compliance

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

http://www.nrel.gov/docs/fy12osti/52905.pdf
Technical Accomplishment: Biodiesel Catalyst Durability Study

- Major collaboration with 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 observed for NOx
- Alkali metals may be affecting DOC performance
Modern cars use adaptive learning to optimize engine control for different fuels (oxygen and energy content).

Adaption affects emissions and fuel economy.

Mid-level ethanol blends (E20-E50) are becoming more common.

Nine cars (2002-2011) tested on E40 – after adaption on either E10 or E76.

Older FFVs may not readily adapt to E40 – they are set up to adapt to E10 or E70-E85.

More modern FFVs adapted rapidly – with the time of a 3 phase LA92 emission test.

Technical Accomplishment:

Performance of Hydrocarbon Renewable Diesel Fuels

- Commercial and prototype 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 (85%+)

Terpenoid-Derived