NATIONAL RENEWABLE ENERGY LABORATORY

Quality, Performance, and Emission Impacts of Biofuels and Biofuel Blends

Vehicle Technologies Program Merit Review - Fuels and Lubricants Technologies

Bob McCormick

May 10, 2011

Washington, DC

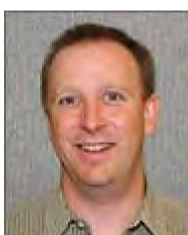
Project ID: FT003

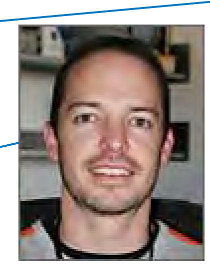
Team Members











Teresa Alleman
Jon Burton
Earl Christensen
Gina Chupka
Wendy Clark
Lisa Fouts
Xin He
Keith Knoll
Mike Lammert
Jon Luecke
Barbara Myers
Matt Ratcliff
Matt Thornton
Aaron Williams
Janet Yanowitz

Overview

Timeline

Start date: Oct 2010

End date: Sept 2011

Percent complete: 66%

Program funded one year at a time

Budget

Total project funding

FY10: $1.8 M

FY11: $1.6 M – estimated

NBB CRADA provides around $750K per year to cost share biodiesel research

Barriers

VTP MYPP Fuels & Lubricants Technologies Goals

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

Partners

- National Biodiesel Board and member companies
- Manufacturers of Emission Controls Association and member companies
- Engine Manufacturers Association® and member companies
- Coordinating Research Council® and member companies
- Colorado School of Mines
- Oak Ridge National Laboratory
- State of Colorado

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 RFS requirements

Goals are solving problems for current biofuels and early identification of problems for future/proposed biofuels – valuable information for planning future R&D

1. Biofuel quality:
   - Need for ASTM standards to help ensure quality in the market place
   - Need for new and improved test methods for biofuels and blends
   - Storage stability and handling issues for new fuels are unknown
   - Low-temperature operability for new diesel fuels has not been researched
2. Inadequate information on engine durability and emission control equipment:
   - Effect of biofuel and impurities on materials and catalysts
   - Impacts on lube oil performance are poorly quantified

4. Poor understanding of air quality impacts:
   - No emission data for newer technology engines
   - Limited data on toxic compound and PN emission effects

Approach/Strategy

- Examining the broad scope of biofuels, from ethanol and biodiesel to next generation oxygenate and hydrocarbons
    - High level screening of new biofuels – future work requiring more detailed study will depend on results
- Measure quality and performance properties, compatibility with engines, lubricants, and emission controls; and impacts on emissions
- Research projects in many different areas: chemical analysis, storage stability, low-temperature operability, volatility, materials compatibility, impurity effects, and emissions
- Statistical analysis of results, and thermophysical property modeling of low-temperature performance and volatility
- Industry collaborations guide our work to be relevant, while collaborations with other labs and universities broaden our effective capability

Milestones

Month/Year	Milestone
Jun-10	**Wintertime Biodiesel Blend Quality Survey.** Forty Bxx blends from public pumps around the United States. Samples generally met the requirements of ASTM D7467, the specification for B6 to B20 blends, however 22% failed for oxidation stability.
Jun-10	**Biodiesel Ash Impacts on DPF Durability.** An accelerated test was used to assess how Na, K, and Ca that may be present in B20 affect durability of 3 different DPFs. The results showed no degradation in the thermal shock resistance of a cordierite DPF after exposure to 150,000 miles of biodiesel ash.
Sep-10	**Biodiesel Effects on PM Size/Number Emissions.** An FMPS instrument was applied to measure the impact of biodiesel, ULSD, and DPF on PM size number emissions.
Sep-10	**Biodiesel Impact on Toxic Compound Emissions.** A novel mass-spec ionization method that is specific for nitro-compounds was employed to measure the impact of biodiesel, ULSD, and DPF on nitro-PAH and other emissions. Blending of biodiesel generally reduced these emissions.
Nov-10	**Effect of saturated monoglycerides on biodiesel low-temperature performance.** A study showing how saturated monoglycerides can negatively impact biodiesel cold weather performance was published.
Mar-11	**Ethanol Blender Pump Fuel Quality Survey.** Fifteen blender pump stations were sampled in July 2010. Conventional gasoline, FFV Fuel, and the two lowest blends were collected. Fuel properties were compared to the D4814 and D5798 specifications.
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 BOBs.
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 AO or stable B100
Aug-11	**Impact of biodiesel ash forming constituents on SCR catalyst performance.** Effects of Na and K on both LD and HD configurations are being measured in accelerated tests.

List of Technical Accomplishments

1. **B20 DOC/DPF/SCR Durability Research**
2. **Saturated Monoglyceride Effects on Biodiesel Low-Temperature Performance**
3. **Properties of Biomass-Derived Oxygenate-Gasoline Blends**
4. **Levulinic Acid Esters as Diesel Blend Components**
5. **FFV Emissions with Blender Pump or Co-Mingled Fuels - ongoing**
6. **Initiated measurement of biodiesel lube oil dilution in both LD and HD systems with active regeneration - ongoing**
7. **2009/2010 Winter Biodiesel Blend Survey**
8. **Ethanol Blender Pump Survey**
9. Developed 2-D GC method for measuring biodiesel and diesel fuel dilution in lube
10. Emission Testing of B20 in Transit Buses - ongoing
11. PM Size/Number Emissions
12. New Analytical Methods for Impurities in Fuel and Toxics Emissions - ongoing

Presented Today (items 1–4)

See Technical Backup Slides (items 5–8)

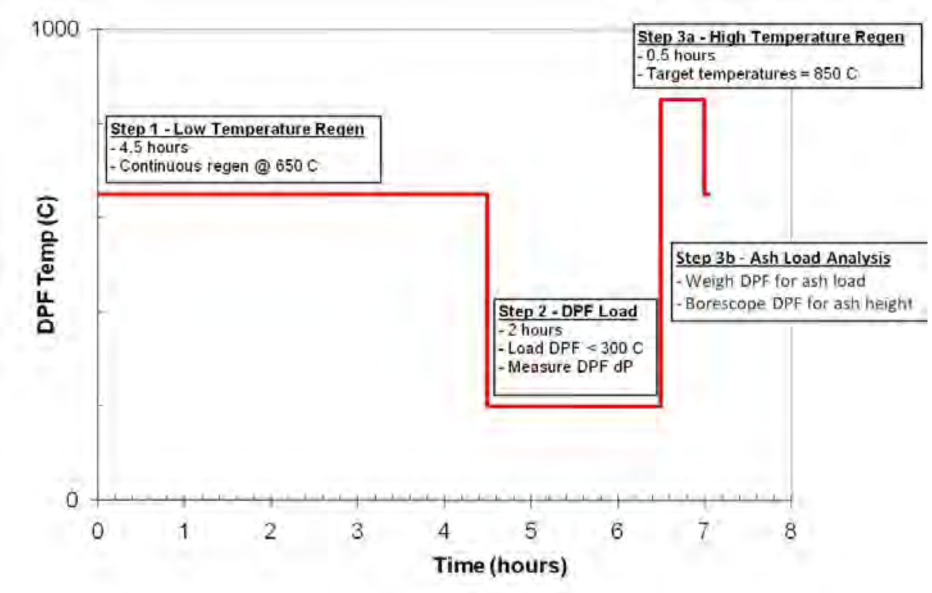
Technical Accomplishment: B20 DOC/DPF/SCR Durability Research

- Do metals at current limits impact performance or durability?
  - *5 ppm max Na+K and 5 ppm max Ca+Mg*
- Accelerated method for exposing emissions control devices to 435k miles of biodiesel ash
  - *Doping fuel with 7 ppm K, 21 ppm Na, and 24 ppm Ca accelerates ash exposure*
  - *Test cycle simulates DPF time/temperature history*

Total Ash Exposure for B20 at ASTM limits
150k miles ~ 232 grams (77 hr)
435k miles ~ 674 grams (222 hr)

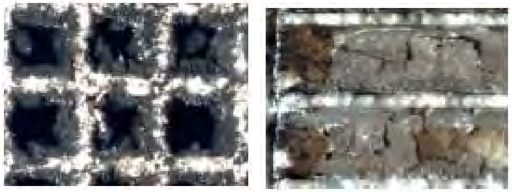
Catalyst parts donated by MECA

Test engine donated by Caterpillar®

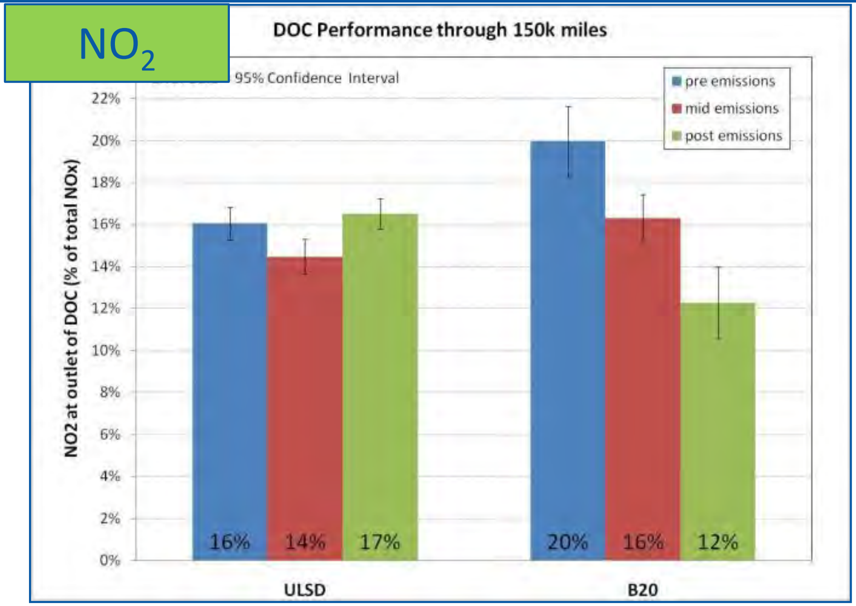


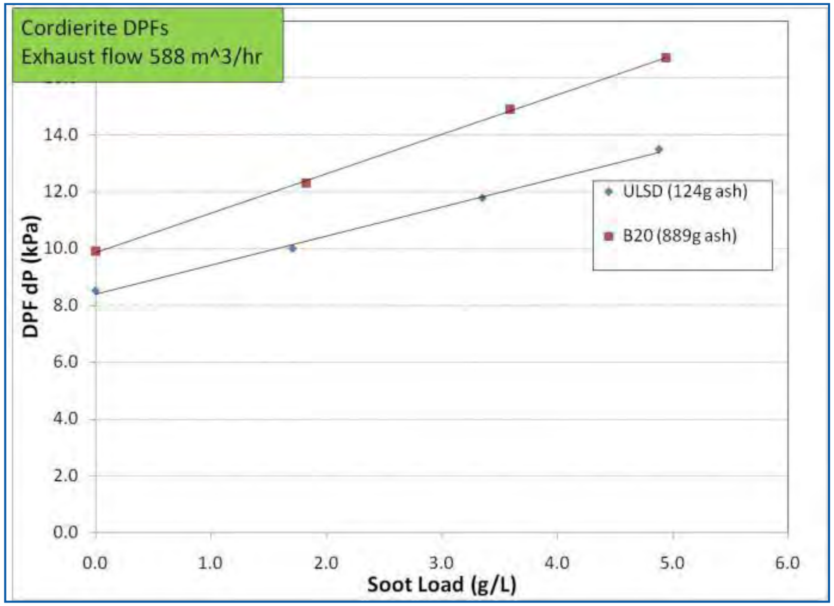
Technical Accomplishment: B20 Impact on DOC and DPF

- DOC activity measured at simulated 150k miles
  - No change in CO conversion
  - 7% reduction in HC conversion
  - 8% reduction in NO_2:NOx ratio
- Inlet section for B20 DOC showed signs of washcoat cracking
  - 1% Na in the washcoat of inlet section



- DPF at 150k miles shows <1 kPa backpressure increase
  - Cordierite showed no change in thermal shock resistance parameter
- DPF operated to 435k miles shows 3 kPa backpressure increase
  - No ash cleaning at 150k mile intervals
  - Thermal shock resistance parameter reduced by 69%

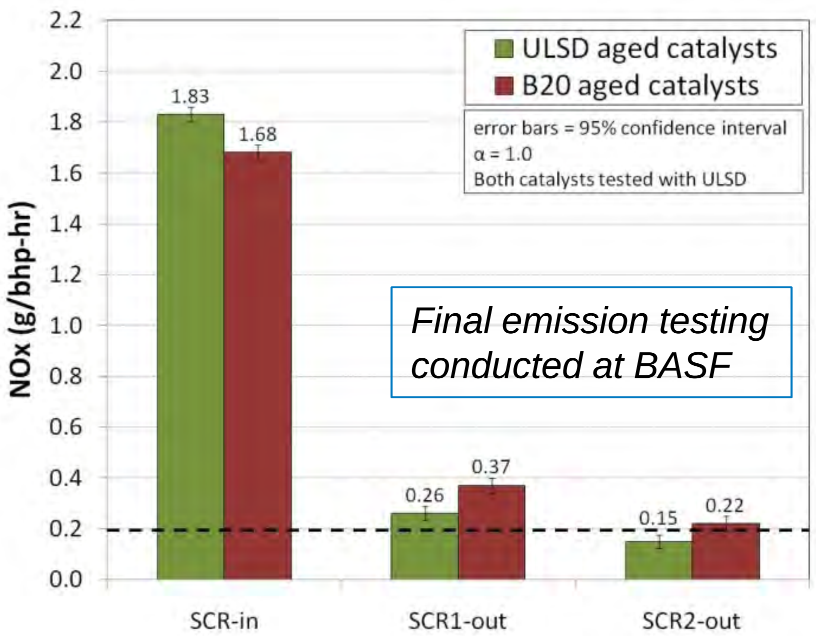




Technical Accomplishment: B20 Impact on SCR Activity

- SCR tested in HD configuration (DOC-DPF-SCR)
- Catalysts emission tested on HDT after simulated 435k mile exposure
- Biodiesel aged catalysts experienced significant deactivation
    - FUL at specification limit
- Potentially caused by alkali metal salt volatilization from DPF
    - Potassium salts more volatile than sodium – but K methoxide rarely used in biodiesel production
- Ongoing follow up examining Na and K separately
- LD (SCR-DPF) and HD (DPF-SCR)

Industry partners: Caterpillar, Ford, NBB, Umicore, BASF Catalysts LLC, MECA, EMA



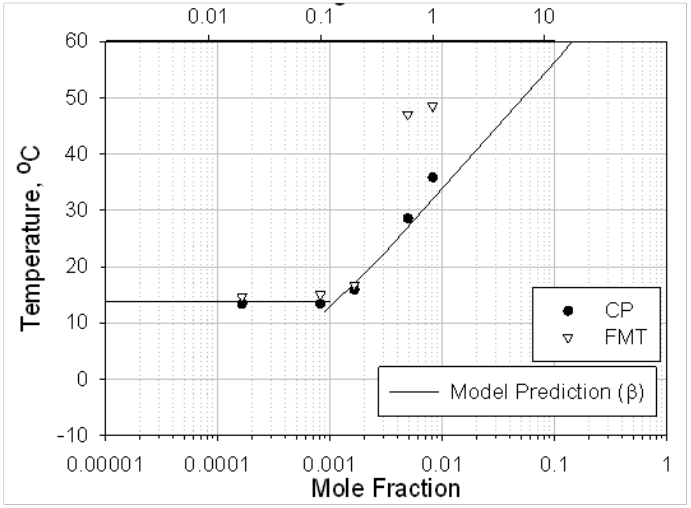
Williams and others, SAE 2011-01-1136

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

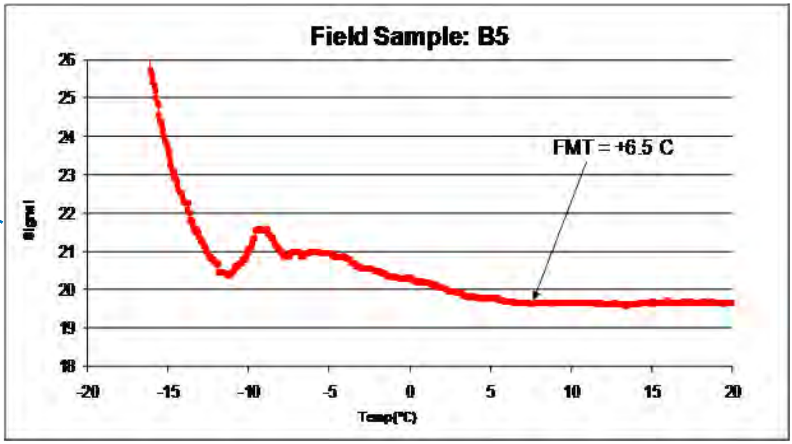
Ideal solution model predicts SMG affect on CP

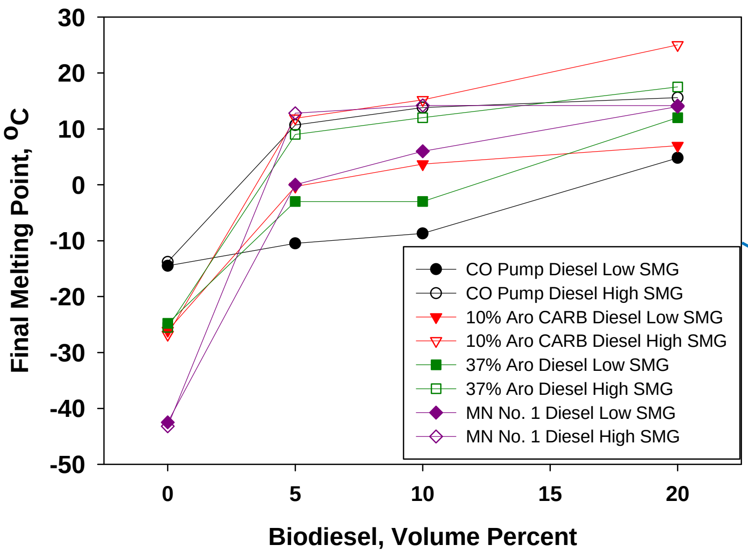
- A single component precipitates at the CP
- The melting point (T_m), heat of melting (ΔH_m) and concentration of component (x) determine the CP for the solution

$$\ln \frac{1}{x} = \frac{\Delta H_m}{R T_m}\left(\frac{T_m}{T} - 1\right)$$



High final melting point observed in real-world diesel causing dispenser filter clogging

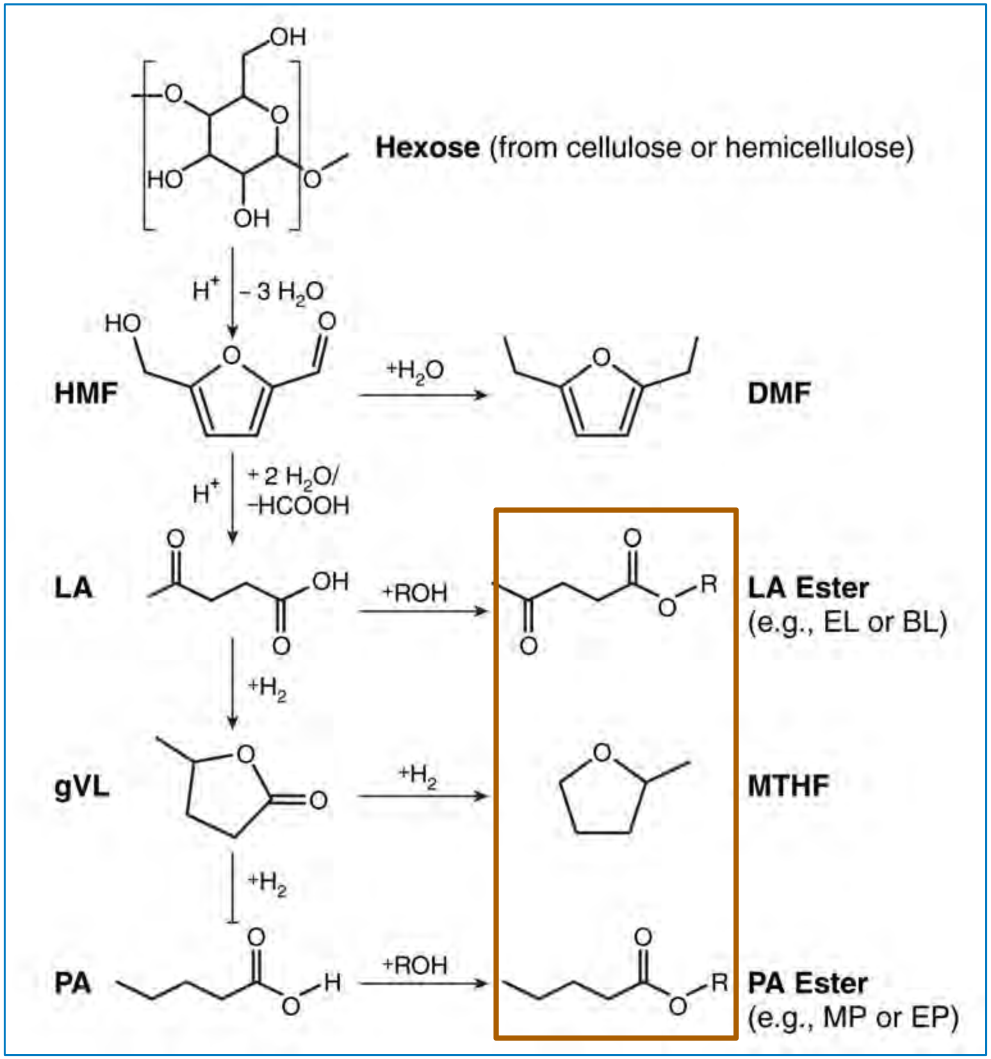




Diesel fuel properties shown to have significant effect on SMG solubility temperature

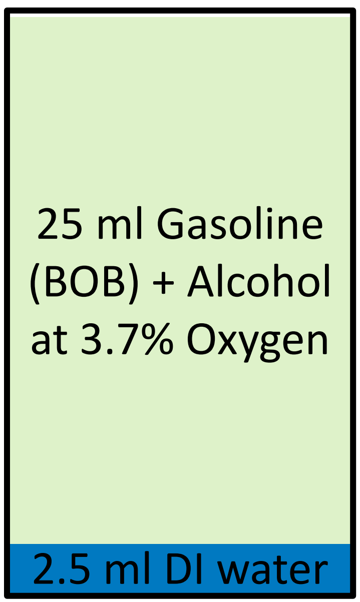
Making Oxygenates from Biomass

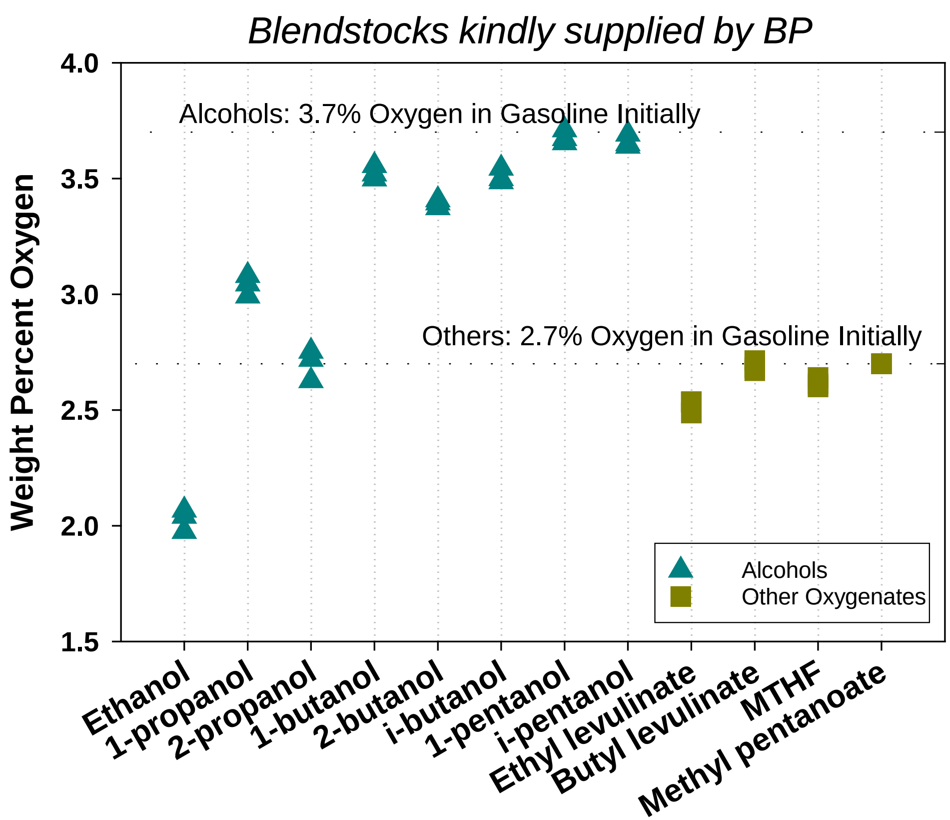
- Biomass has a high oxygen content
  - O/C molar ratio of 0.6
- Hydrocarbons may be preferred… but the most economical approach may prove to be oxygenates
- Alcohols from various approaches:
  - Gasification/syngas conversion *($1.85/gal ethanol projected)*
  - Biochemical plus fermentation
- Oxygenates from acid hydrolysis and upgrading:
  - Levulinc acid esters (*15¢/lb projected)*
  - MTHF
  - Pentanoate esters
- *We are taking a very high level look at performance properties and emission impacts*



Technical Accomplishment: Oxygenate-Gasoline Water Interaction

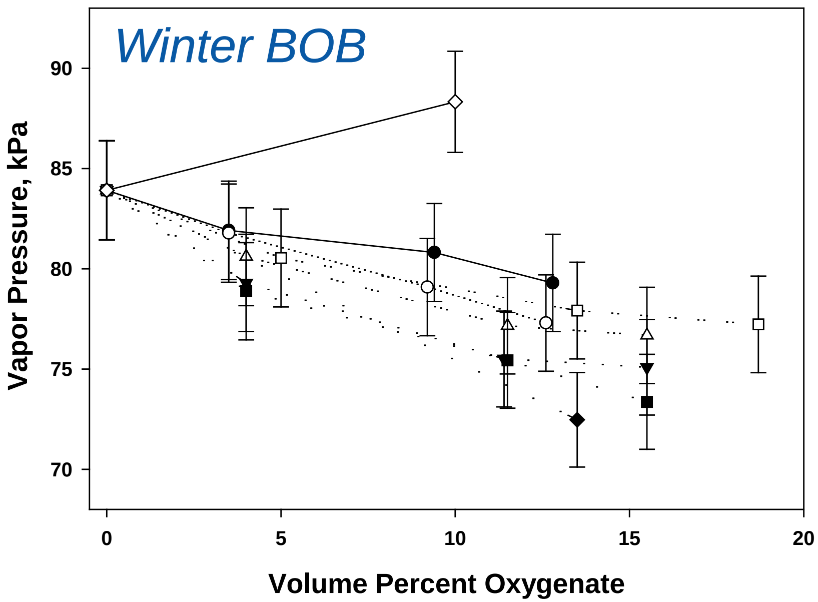
- C2 to C5 alcohols blended in gasoline at 3.7 wt% oxygen
  - Level allowed by EPA waivers to the substantially similar rule
- Other oxygenates blended at 2.7% oxygen
  - MTHF (an aliphatic ether) allowed by subsim rule, other oxygenates are not subsim

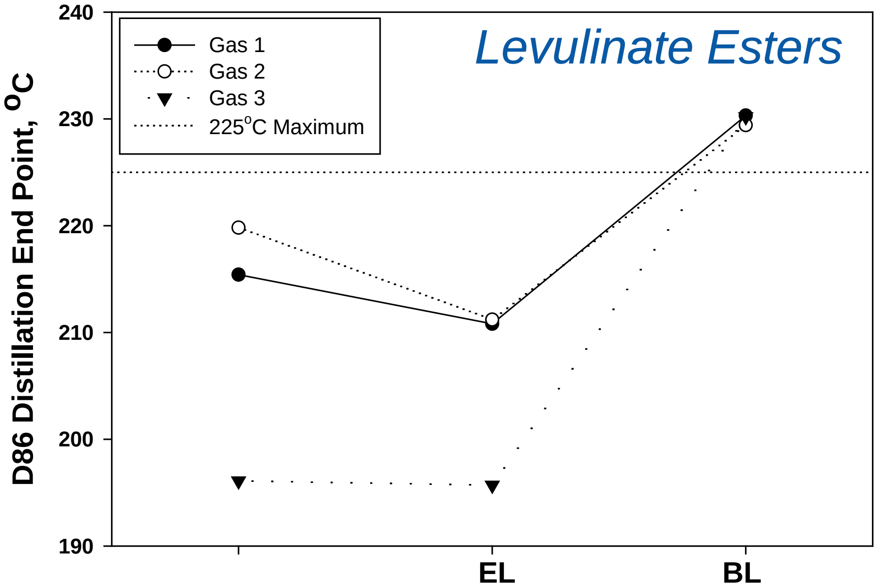


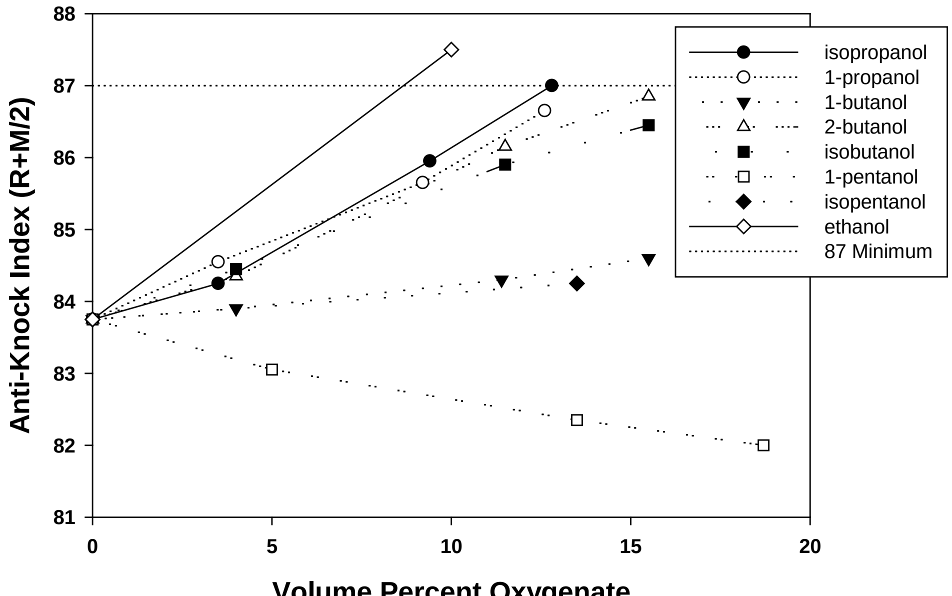


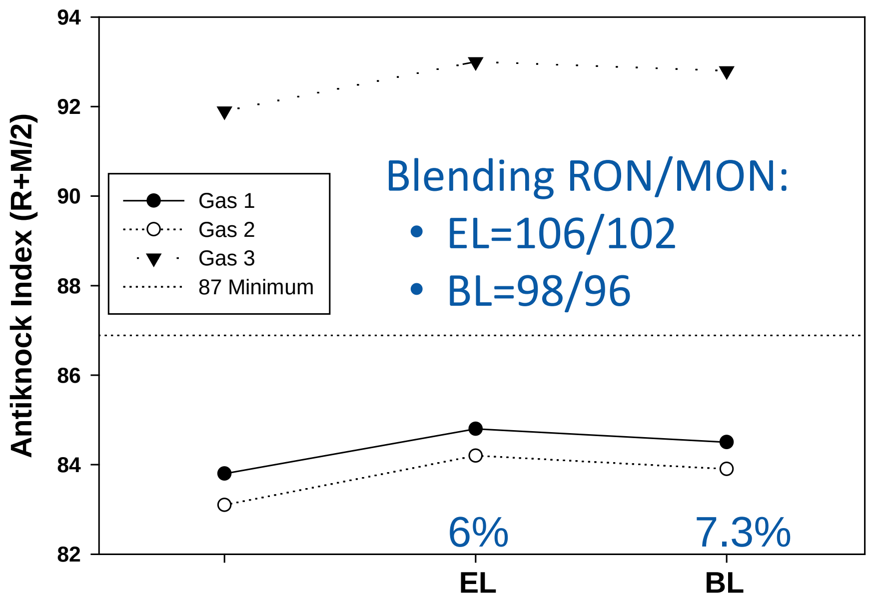
Compound	Boiling Point (°C)
Gasoline	27-225
Ethanol	78
1-Propanol	97.2
2-Propanol	82.3
1-Butanol	117.7
i-Butanol	107.9
2-Butanol	99.6
1-Pentanol	137.8
i-Pentanol	132
MTHF	78
Ethyl levulinate	206
Butyl levulinate	237.5
Methyl pentanoate	126

Technical Accomplishment: Oxygenate Effects on Performance Properties





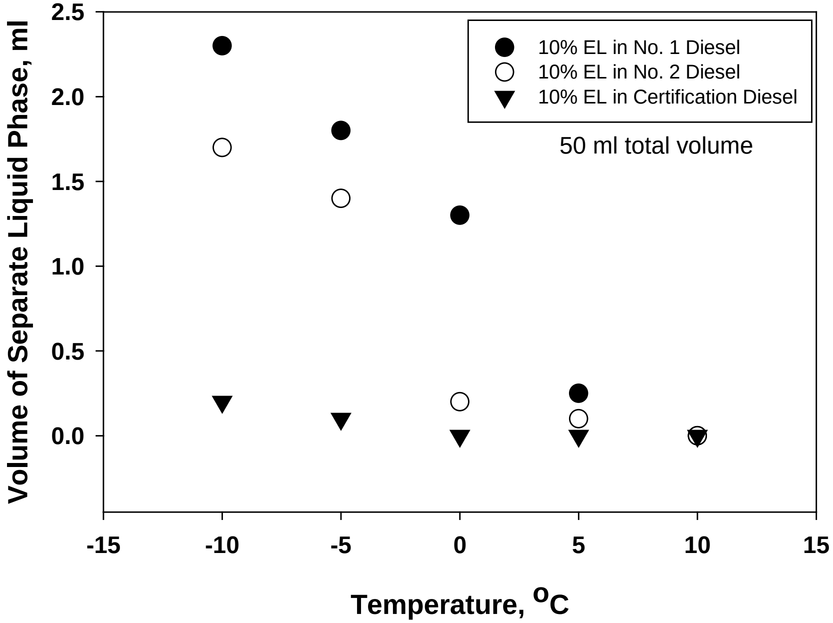


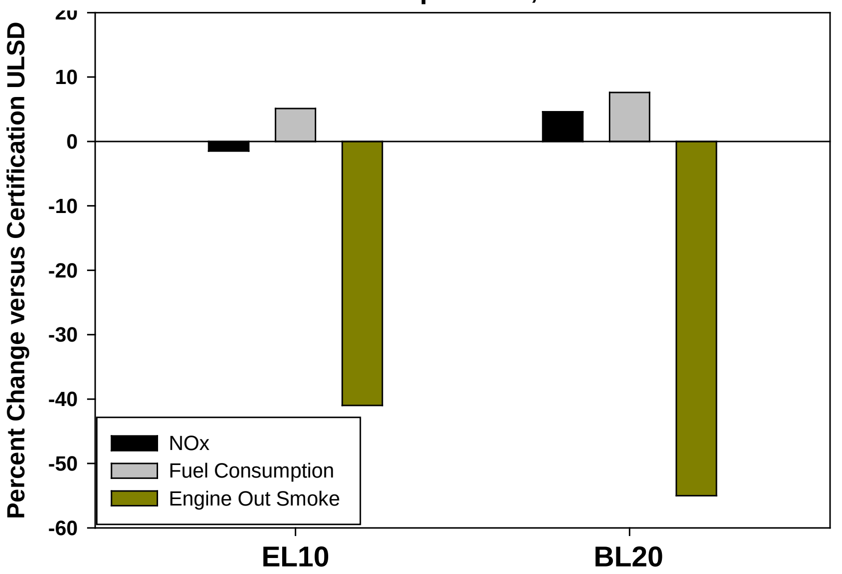


Technical Accomplishment: Levulinic Acid Esters as Diesel Components

- Ethyl ester poorly soluble in diesel fuel, up to 8% can be extracted into water
- Butyl ester was soluble and had no effect on cloud point, very little extracted into water
- Enhanced both lubricity and conductivity
- Require cetane additive (2-ethyl hexyl nitrate) – 0.79 v/v% in ester
- Emission testing in 2008 MY Cummins ISB over HDT
  - Large reduction in PM – high oxygen content
  - NO_x effect inconsistent, likely because of cetane enhancer
- Use of these esters as diesel blend components seems challenging

Industry partners: Mead-Westvaco Corporation and Trenton Fuel Works, LLC





Collaboration and Coordination with Other Institutions

B20 DOC/DPF/SCR Durability Research

- MECA and member companies
  - Umicore
  - BASF Catalysts, LLC
- Caterpillar
- Ford
- NBB (cofunding)
- EMA and member companies
- ORNL

Saturated Monoglyceride Effects on Biodiesel Low-Temperature Performance

- NBB and member companies (cofunding)

Properties of Biomass-Derived Oxygenate-Gasoline Blends

- National Bioenergy Center (NREL)

Levulinic Acid Esters as Diesel Blend Components

- Mead Westvaco
- Trenton Fuel Works

FFV Emissions with Blender Pump or Co-Mingled Fuels

- State of Colorado (cofunding)

2009/2010 Winter Biodiesel Blend Survey

- NBB and member companies

Ethanol Blender Pump Survey

- CRC and member companies (cofunding)

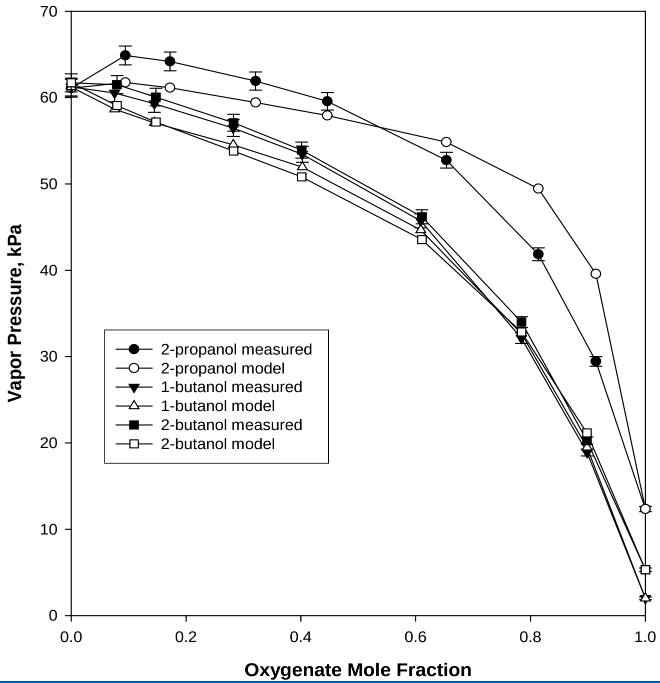
New Analytical Methods for Impurities in Fuel and Toxics Emissions

- Colorado School of Mines

Proposed Future Work

Plan significant expansion of thermodynamic modeling of phase equilibrium:

- Volatility of metal salts in emission control equipment
- Precipitation of solids in fuel at cold temperature
- Vapor pressure and distillation of oxygenate gasoline blends



B20 DOC/DPF/SCR Durability Research

Impacts of Na and K separately

Metals effects for LD and HD configurations

Biodiesel Low-Temperature Performance

Effect of mixed saturated and unsaturated monoglycerides, water, and other impurities

Diesel fuel property effects on SMG solubility

Biomass-Derived Oxygenate-Gasoline Blends

Assess gasoline blend properties for viability of oxygenates

Basic emission testing for viable oxygenates

Mixed-alcohols similar to OBP thermochemical platform

FFV Emissions with Blender Pump Fuels

Complete emission testing of 6 additional FFVs

Biodiesel Lube Oil Dilution

Complete analysis of HD lube oil samples

Measurement of LD lube oil dilution study using MAD

2011 B100 Quality Survey – including detailed analysis of impurities present

Emission Testing of B20 in Transit Buses

Test 2 additional buses

Fuel Butanol ASTM Standard – support development at ASTM

Summary

- Guidance from last years AMR has improved the quality of the NREL NPBFL activity
- Studies of how biodiesel impurities impact engine and catalyst performance, as well as quality surveys, will expand markets for biodiesel
- Examination of biodiesel impacts on lube oil will provide industry with valuable information and serve as a template for future studies on lube oil compatibility with other fuels
- High level testing of a range of biomass-derived oxygenates will provide DOE and industry with guidance on viability of these fuels
- Research on high-level ethanol blends in FFVs will demonstrate the potential of this approach for petroleum displacement

Technical Backup Slides

Technical Accomplishment: Blender Pump Fuel Impacts on FFV Emissions

Impetus:

- Blender pump re-fueling, even for properly functioning FFVs, may result in unintended increases in tailpipe emissions
- FFV algorithms were designed for E0/E10 or nominal E85 fueling. Blender pump fueling may result in loss of adaptive fuel:air control

Approach:

- *Collaborate with state of Colorado* emissions lab – CDPHE to provide all vehicle testing and regulated emissions
- Include 9 FFVs from two model year groups (2001-2006 / 2007-current)
  - Measure fully adapted emissions on E10 & E85
  - Measure hot start emissions following E40 “blender pump” fueling
  - Measure adapting & adapted emissions on E40

Status:

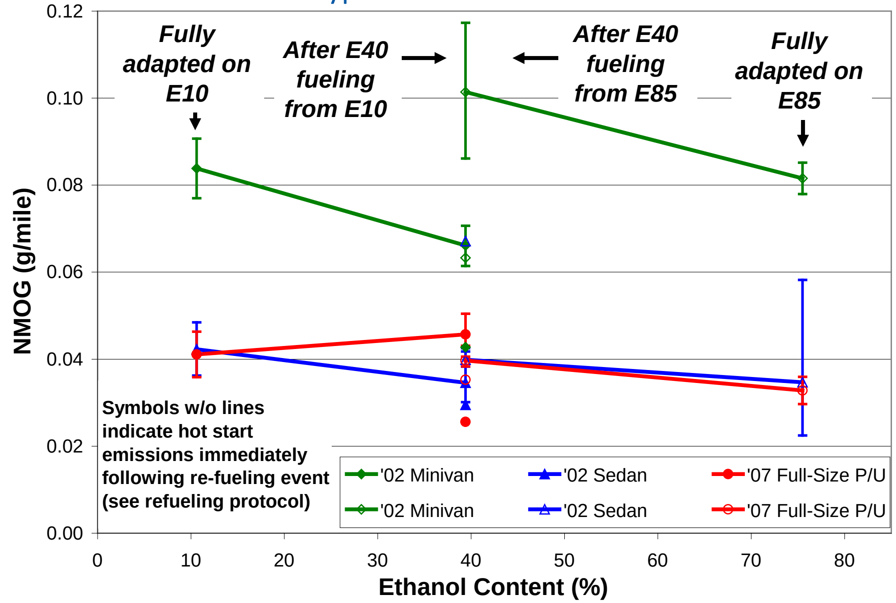
- Three vehicle complete
- Next three vehicles procured – will begin test in March
- Three additional vehicles to be tested in May/June timeframe

Technical Accomplishment: Emissions & Fuel Economy on LA92 Drive Cycle

Emissions Trends:

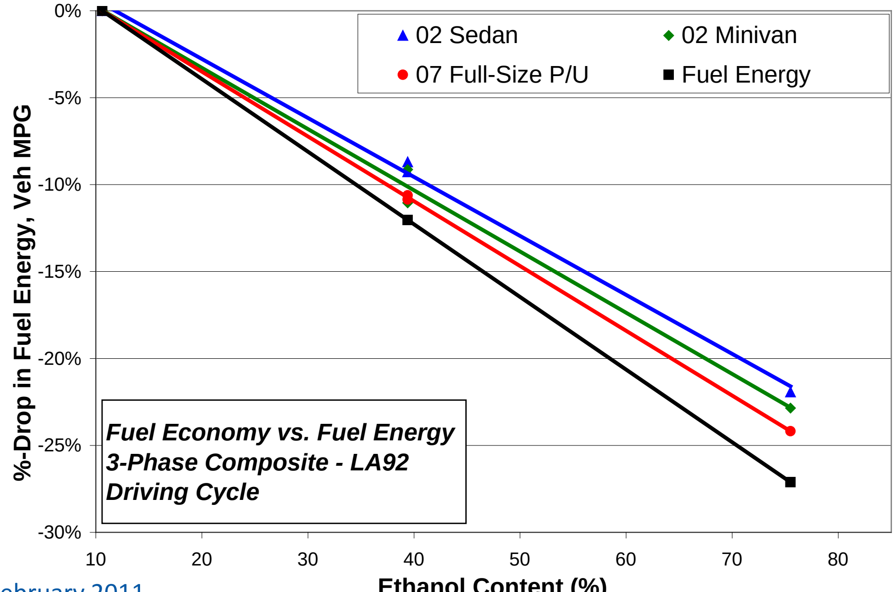
- One vehicle ('02 Minivan) exhibited poor adaptation following blender pump fueling with E40.
- Two vehicles ('02 Sedan and '07 P/U) showed good adaptation to blender pump fueling with E40.
- Emissions followed expected trends with increasing ethanol:
    - NMOG & CO both reduced
    - NO_X either reduced or flat
    - aldehydes increased.

NMOG trends typical of other measured emissions



Fuel Economy:

- As reported elsewhere*, loss tracked slightly below energy content of fuel
- Potential influence variables:
    - charge air cooling
    - combustion efficiency
    - spark advance

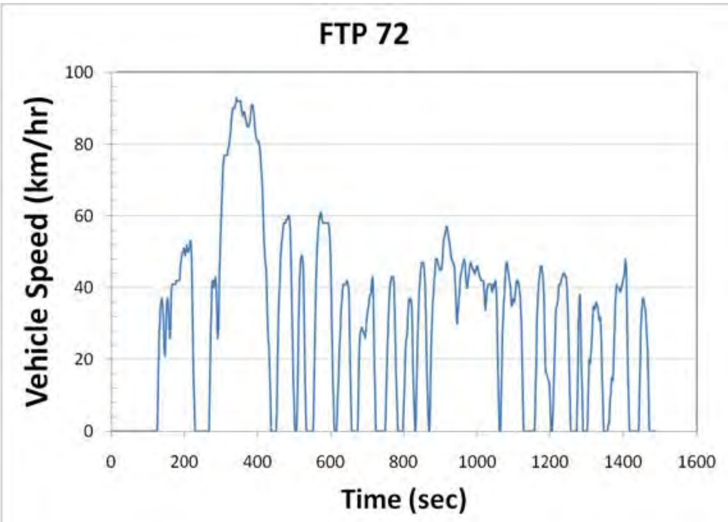


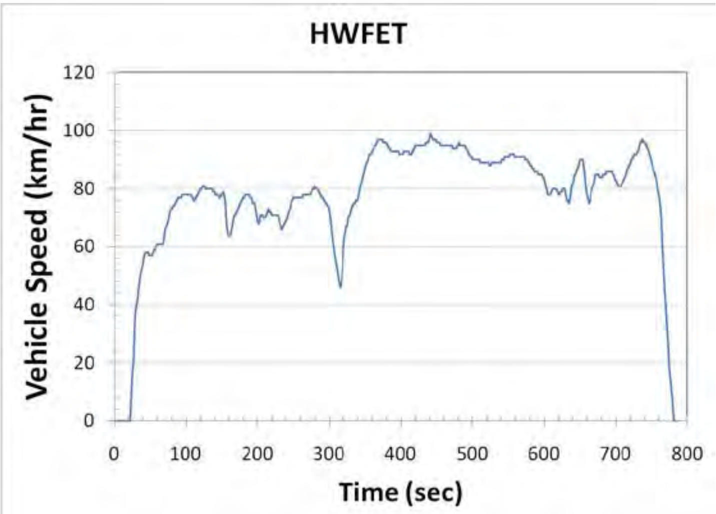
* *Ethanol - the primary renewable liquid fuel*, Datta, et. al., J. Chem Technol Biotechnol, February 2011.

Technical Accomplishment: Biodiesel Lube Oil Dilution

- Active DPF regeneration through post injection can result in fuel oil dilution
- Higher boiling point of biodiesel can increase propensity for lube oil dilution
- 2010 VW Jetta operated on mileage accumulation dyno for 4000 miles
    - B20 and ULSD
    - FTP72 (more frequent regen)
    - HWFET (less frequent regen)
- Lube oil samples collected at 400 mile intervals
- Samples analyzed for fuel dilution, soot, TAN, TBN, viscosity, wear metals and HFRR

2010 VW Jetta – 2.0L TDI
Tier II Bin 5, DOC+DPF+LNT





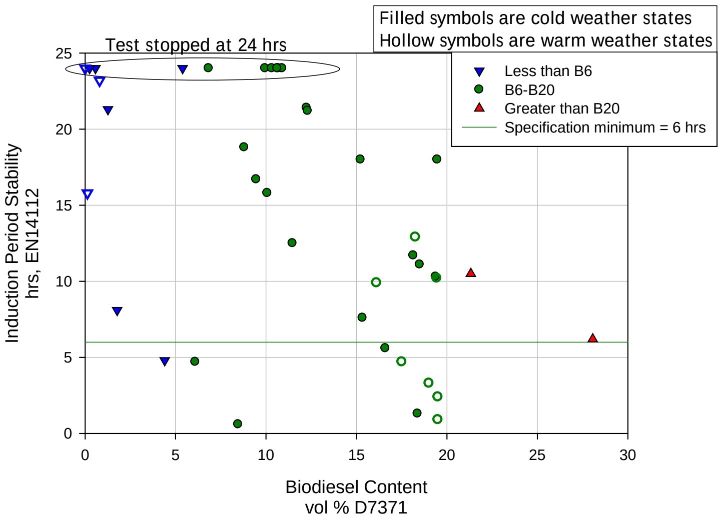
Technical Accomplishment: Wintertime B6-B20 Survey

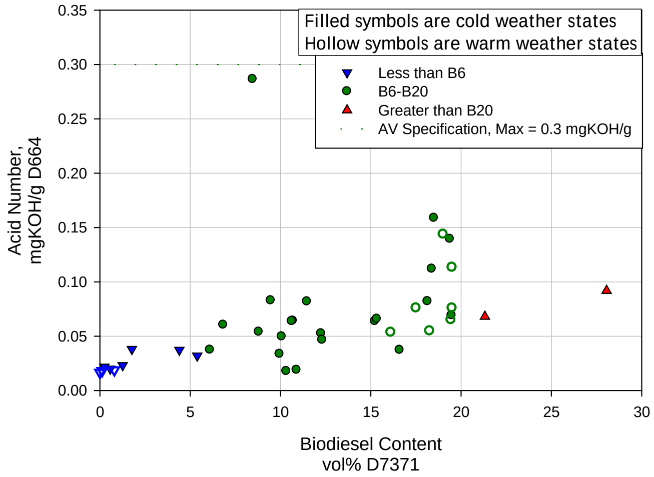
Accomplishment

Completed collection of 40 wintertime B6-B20 blends across US to assess quality at the pump, 75% of samples were from states with 10th percentile ambient temperature below -12 C.

Significance

- First biodiesel blend quality survey conducted since D7467, B6-B20 specification, was adopted.
- Milestone due 6/30/10.
- Continued problems with meeting oxidation stability.
- Data might support lowering current AV specification.
  - Enabled by improved detection limits in test method
  - Strong desire from OEMs to have AV as low as possible





Accomplishment

- Collected samples from 15 stations in 8 states
- Collaboration with CRC

Significance

- First survey of blender pumps to assess quality – there is no specification for fuels with ethanol content above gasoline, but below E85
- Collected base gasoline, E85, and 2 lowest blends offered (typically E20 and E30)
- Gasolines varied from E0 to E10
- E85 samples typically met the specification
- Exx blends "looked" more like gasoline than E85 and would not meet the D5798-10 specification