Quality, Performance, and Emission Impacts of Biodiesel Blends

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Vehicle Technologies Program Merit Review
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Overview

Timeline
Start date: FY05
End date: FY12
Percent complete: 60%

Budget
• Total project funding
  – $9.5 M FY05-FY09 DOE
  – $4.8 M FY06-FY09 NBB
    – $3.4 M funds-in CRADA
    – $1.4 M cost share
• FY08: $1.8 M
• FY09: $1 M under CR

Barriers
FCVT 2006-2011 MYPP
  – Infrastructure compatibility
  – Inadequate data for fuel property effects on combustion and engine optimization
  – Inadequate data for fuel effects on emissions and emission control system impacts.
  – Long-term impact of fuel and lubricants on engines and emission control systems

Partners
• National Biodiesel Board and NBB member companies
• Cummins
• Caterpillar
• Manufacturers of Emission Controls Association
• Engine Manufacturers Association
• Coordinating Research Council
• Members of ASTM Biodiesel Task Force
• Colorado School of Mines
• Southwest Research Institute®
Address and resolve technical issues that are preventing expanded markets for biodiesel blends

1. **Biodiesel quality:**
   - Need for ASTM standards to help ensure quality in the market place
   - Need for new and improved test methods for B100 and blends
   - Some poorly understood factors affecting low-temperature operability

2. **Poor understanding of how biodiesel impacts emission control devices:**
   - Both short term performance and long-term durability of DPF, SCR, and LNT systems
     - Associated lube oil dilution issues

3. **Inadequate information on long-term engine durability impacts:**
   - Engine dyno durability tests
   - Quantitative studies comparing petro and biodiesel over multiple years
   - Impacts on lube oil performance are poorly quantified

4. **Poor understanding of air quality impacts:**
   - Early studies showed biodiesel blends increasing NO$_x$ emissions – leading state regulatory agencies to limit biodiesel use
   - Limited data on toxic compound emission effects
Multiple, credible life-cycle analyses show that biodiesel displaces imported petroleum. There is an adequate resource to displace 5% of petroleum diesel, at a minimum. R&D to increase oil yield from existing crops, develop new crops, and to develop non-crop feedstock sources (algae, trap grease,...) may dramatically increase this resource. Installed production capacity for biodiesel already exceeds 5% of the on-highway diesel market. Biodiesel also reduces greenhouse gas emissions relative to petroleum – even when worst case scenario indirect land-use effects are included (in some analyses).
Milestones

Task 1 FY08 Milestone:
• Revision and update of Biodiesel Handling and Use Guide, postponed from FY07. (September 2008)
  – 3rd edition was downloaded 32,000 times in 2008, 4th edition has been downloaded 2800 times as of March 2009

Task 2 FY08 Milestone:
• Complete a detailed study of the performance and compatibility of biodiesel with urea SCR NOx emission control system. (September 2008)
Approach

Applied development work focused on fuel chemistry and empirical studies of full scale systems

- Performance testing and chemical analysis of commercial fuels
  - Development of new and improved fuel testing methods
- Engine and vehicle dynamometer testing
  - Emissions, engine and emissions durability
  - Low-temperature operability
- Quantitative, controlled in-use fleet testing
- Meta-analysis of large datasets from published literature
- Industry partners or broad industry participation in work group or steering committee
Technical Accomplishments

ASTM Approves Specifications for Biodiesel Blends

• Allowance of up to 5% biodiesel in D975 diesel fuel and D396 heating oil
• New specification for B6 to B20 blends for diesel engines: D7467
• Data from this program was instrumental in passing these after 10 years of discussion:
  – B100 and B20 quality surveys
  – Oxidation stability study
  – Low-temperature operability study
  – Test method development and improvements

UL Approves Use of B5 In All Equipment Listed for Diesel Fuel
Technical Accomplishments

**Completed Nationwide B20 Quality Survey**

- 32 samples collected in 25 states from public pumps and fleets
- Samples acquired before D7467 was in effect
- Generally good compliance with D7467 except for oxidation stability (36% of samples failing)
- Average dissolved water content of 130 ppm, water interfacial tension of about 12 mN/m
- All pumps were labeled for B20 but 40% of samples were B11, B5, or B2.
Validated Low-Temperature Operability and Minor Species Tests for Biodiesel Blends

- Collaboration with CRC, EMA, and NBB – in support of ASTM and setting of blend specifications
- Precipitates in biodiesel blends have been observed above the cloud point
  - Requires long cooling time (8-16 hr)
  - Can occur for on-specification fuel
- Exact chemical character poorly defined
- Low Temperature Operability Study
  - CRC Study DP-2a-07
  - Validate low-temperature tests for biodiesel blends (cloud point, CFPP, CSF)
  - Validate cold soak filtration test to eliminate minor components
  - Actual testing of vehicles (HD trucks) at low temperature to determine operability limits

Courtesy of John Chandler
Low-Temperature Operability Validation for Biodiesel Blends -II

- Tests performed at Imperial Oil, Sarnia, ON: 4 B5 and 4 B20
- Class 8 trucks with roughly 25% to 30% market share for each engine manufacturer (Caterpillar, Cummins, DDC)
- Vehicle inertia of 80,000 lb

Conclusions:
- Cloud point is a good estimate of minimum operability temperature for blends up to B20 from B100 with CSFT<200 sec
- For the single B100 tested with CSFT >720 sec:
  - For B5 blend operability limit was at or below cloud point
  - For B20 blend failure to operate at and above cloud point was observed for one vehicle design
- Final report (CRC Report No. 650):
Working to identify minor species causing cold weather issues

- No fundamental understanding of the cause of precipitates above the cloud point in biodiesel blends
- No fundamental understanding of what causes B100 to have high cold soak filtration time
- Goal is to be able to quantify all minor species that might precipitate or form emulsions above cloud point
- Laboratory cold soaking and centrifugation produces complex mixtures
- Developing advanced analytical tools to use in concert with cold soak tests and other sample treatments (MS/MS, MALDI-TOF, others)

- Matrix-Assisted Laser Desorption Ionization-Time of Flight mass spectrometry
- Produces primarily molecular ions and enhances separation of minor species
Technical Accomplishments

Lower Detection Limits for Metals and Phosphorus in B100

• Metals in B100 derive from the manufacturing process (Na, K, Ca, and Mg), phosphorus can be present in vegetable oil feedstocks.
• They are a major concern for DPF durability and meeting the EPA required useful life requirements.
• May also be of concern for SCR systems.
• Metals at detection limit of current methods are high enough to be of concern.
• Modified ICP-AES instrument leads to much lower detection limits than available in current ASTM methods.
• New method DL:
  • Na&K: 100 ppb
  • Ca&Mg: 10 ppb
  • P: 500 ppb

80% of samples show Na and K below detection limit
Improved method lowers DL by factor of 10

Alkali observed with modified method are potentially contamination from glass storage bottles
Distilled B100

Modified ICP results courtesy of William Zaccarelli of Horiba Jobin Yvon
Technical Accomplishments

Full Useful Life Aging of LD NAC/DPF and SCR/DPF Systems Completed

- Parameters:
  - 113 kW, 4 cylinder, common rail, late in-cylinder injection
  - B20
  - Vehicle emission tests, ECS mounted on engine dyno for 120,000 mi simulated aging

- NAC system achieved Tier 2 Bin 5 emission levels at full useful life (120K)
  - 20% degradation of NO\textsubscript{x} conversion efficiency at full useful life

- SCR System did not achieved Tier 2 Bin 5 emission levels at full useful life (120K)
  - 30% degradation of NO\textsubscript{x} conversion efficiency at full useful life
  - SCR manufacturer found that performance degradation caused by thermal runaway, not a fuel issue

- Engine measurement show no degradation of engine parts – after 2x useful life aging

- Lubricant testing shows biodiesel content up to 10% for NAC system – analysis ongoing
Technical Accomplishments

**Short-Term Testing of HD Urea SCR System Completed**

- Parameters:
  - 2002 Cummins ISB retrofitted with DOC/DPF – SCR (Fe-Zeolite)/NH₃ Slip
  - Air assisted urea injection
  - 8-mode steady-state test
  - HC inhibition after 35 hr exposure
- Short term test shows no difference in NOₓ reduction performance of B20 and ULSD
- Significantly less HC inhibition for B100
  - Lower engine out HC emissions
  - Quicker recovery to steady-state NOₓ conversion after increasing temperature
  - Sample collected for HC speciation – analysis ongoing
- Initiating collaboration with LD OEM to improve understanding of these effects
Technical Accomplishments

Completed Additional Study of Biodiesel Affect on PM Reactivity

- Previous studies showed that biodiesel soot is more reactive and has higher oxygen content & more amorphous soot structure
- Engine test results show clear dependence on biodiesel blend level & oxygenate structure
- Impact of Na may be within measurement error
- Collaboration with ORNL will provide detailed characterization and reactivity of soot samples

B10 = 13% faster than ULSD
B20 = 28% faster than ULSD
B100 = 77% faster than ULSD

7ppm Na = 6% faster than 0ppm Na
Decanol = 15% faster than B20
Technical Accomplishments

**Emission Speciation Using GC/EM-MS Reveals Effects on NPAH**

- **Chart** shows engine-out NPAH for SS test of 2004 diesel engine retrofitted with DOC/DPF, DCM extracts of PM from dilute exhaust
- **DOC/DPF** effectively oxidized most NPAH, except 1-Nitropyrene
- **Biodiesel blending** reduced engine-out and DPF-out NPAH
- **B100** increased semi-volatile nitro-compounds emissions (not shown)
- **More volatile nitro-compounds** exiting DPF may not be fully accounted

<table>
<thead>
<tr>
<th>Nitrobenzene</th>
<th>1-Nitropyrene</th>
<th>Engine-out (ng/sample)</th>
<th>DPF-out (ng/sample)</th>
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<tr>
<td>Cert Fuel</td>
<td>123</td>
<td>80</td>
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<tr>
<td>B20 Fuel</td>
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<tr>
<td>B100 Fuel</td>
<td>27</td>
<td>15</td>
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- **Electron-monochromator mass spectrometry**
- **Tune electron energy** to efficiently ionize only nitro-species
• Fuel Quality Focus Area:
  – Chemical analysis and performance testing to show conclusively what minor species cause low-temperature operability issues
  – Oxidation stability study focused on fuel injection equipment compatibility
  – Support ASTM method development and improvement as needed
    • Lower detection limits for metals, improved glyceride method, methods for minor species

• Engine and Emission Control Focus Area:
  – Biodiesel ash effects on DPF and SCR durability
  – Biodiesel emission and performance in DPF equipped engines
  – Lube oil performance impacts, especially in systems with late in-cylinder injection for emission control system regeneration
  – Long-term fleet evaluation with DPF equipped engines
    • Major new study in collaboration with NYC Sanitation Department (Mack/Volvo engines)
  – Testing of biodiesel from new and sustainable sources

• Air Quality Impacts Focus Area:
  – Additional analysis to identify semivolatile NPAH and other compounds observed in speciation study
Future Work: DPF Durability

• Determine if there is a need to lower current ASTM standard for alkali metals in biodiesel. *Does current standard affect ash clean interval or durability of DPF?*

• **Approach**
  – Match total ash accumulation to 150k mile ash clean interval through accelerated test: 30x alkali levels for 110 hours
  – Match total time of exposure to high regeneration temperatures for 150k miles. *Achieve 50 hours regen time by operating at >650 °C for 45 hours and >850 °C for 5 hours*

• Test plan developed with input from NREL, MECA, EMA, NBB and other Industry Stakeholders

• Testing to commence in March 2009

**Engine:** – 2006 C9 ACERT™ loaned by Caterpillar, Tier 3 off-road, 8.8L 300hp

**DPFs:** – 10.5” x 12” (17L) cylinders donated through MECA
  – Cordierite, SiC & AlTi substrates supplied by different mfg.
  – All samples coated to agreed upon loading to ensure consistency

**Fuel:**
– Doped with Na-soap or Na-naphthenate (and other metals)
– 30x spec limits for B100
– B20/ULSD
Summary

• Fuels Technologies biodiesel effort listens to industry stakeholders and supplies unbiased data to address concerns relevant to displacing more petroleum with this biofuel

• Important accomplishments in FY08/FY09 include:
  – Major contributions to passage of biodiesel blend specifications at ASTM
  – Completion of nationwide B20 quality survey
  – Validation of low-temperature operability tests
  – Developing new analytical methods for minor species in biodiesel
  – Lowering detection limits for metals in biodiesel
  – Demonstrating FUL effects of B20 on LD NAC/DPF and SCR/DPF systems
  – Evaluating performance effects of B20 on HD DPF and SCR systems
  – Applying powerful new methods to speciation of compounds in exhaust

• Ongoing and planned projects will reveal HD long-term durability impacts on emission controls and lubricant