Biodiesel Research Update

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Acknowledgment

Office of FreedomCAR and Vehicle Technologies
Fuels Technology Subprogram
U.S. Biodiesel Feedstock Supply Analysis

- 1.7 billion annual gallon existing resource
- Additional 3.5 billion annual gallons by 2015
- Perhaps 10 billion annual gallons by 2030
- Technical barriers:
  - Glycerin
  - Cloud point for animal fat-based fuels
  - Plant breeding and production methods for new crops
- US on-road market: ~40 billion annual gallons

Feedstock analysis from NREL/TP-510-34796, June 2004
Energy Security and Global Warming Benefits

Fossil Energy Ratio (FER) = \[
\frac{\text{Energy Delivered to Customer}}{\text{Fossil Energy Used}}
\]

For soybean-based biodiesel = 3.2 (urban bus assessment)

Fossil energy used in production is similar to petroleum, small fraction of fuel energy-truly renewable

Analysis from NREL/TP-580-24772, May 1998
Biodiesel Quality Specification

- ASTM D6751 specifies the quality of biodiesel to be used for blending in the US
  - Two grades, S500 and S15
  - Notably does not include oxidation stability
  - Currently no standards for biodiesel blends

<table>
<thead>
<tr>
<th>Property</th>
<th>Test Method</th>
<th>Grade S15 Limits</th>
<th>Grade S500 Limits</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash point (closed cup)</td>
<td>D 93</td>
<td>130.0 min</td>
<td>130.0 min</td>
<td>°C</td>
</tr>
<tr>
<td>Water and sediment</td>
<td>D 2709</td>
<td>0.050 max</td>
<td>0.050 max</td>
<td>% volume</td>
</tr>
<tr>
<td>Kinematic viscosity, 40°C</td>
<td>D 445</td>
<td>1.9–6.0°C</td>
<td>1.9–6.0°C</td>
<td>mm²/s</td>
</tr>
<tr>
<td>Sulfated ash</td>
<td>D 874</td>
<td>0.020 max</td>
<td>0.020 max</td>
<td>% mass</td>
</tr>
<tr>
<td>Sulfur</td>
<td>D 5453</td>
<td>0.0015 max (15)</td>
<td>0.05 max (500) % mass (ppm)</td>
<td></td>
</tr>
<tr>
<td>Copper strip corrosion</td>
<td>D 130</td>
<td>No. 3 max</td>
<td>No. 3 max</td>
<td></td>
</tr>
<tr>
<td>Cetane number</td>
<td>D 613</td>
<td>47 min</td>
<td>47 min</td>
<td></td>
</tr>
<tr>
<td>Cloud point</td>
<td>D 2500</td>
<td>Report</td>
<td>Report</td>
<td>°C</td>
</tr>
<tr>
<td>Carbon residue</td>
<td>D 4530</td>
<td>0.050 max</td>
<td>0.050 max</td>
<td>% mass</td>
</tr>
<tr>
<td>Acid number</td>
<td>D 664</td>
<td>0.80 max</td>
<td>0.80 max</td>
<td>mg KOH/g</td>
</tr>
<tr>
<td>Free glycerin</td>
<td>D 6584</td>
<td>0.020</td>
<td>0.020</td>
<td>% mass</td>
</tr>
<tr>
<td>Total glycerin</td>
<td>D 6584</td>
<td>0.240</td>
<td>0.240</td>
<td>% mass</td>
</tr>
<tr>
<td>Phosphorus content</td>
<td>D 4951</td>
<td>0.001 max</td>
<td>0.001 max</td>
<td>% mass</td>
</tr>
<tr>
<td>Distillation temperature,</td>
<td>D 1160</td>
<td>360 max</td>
<td>360 max</td>
<td>°C</td>
</tr>
<tr>
<td>Atmospheric equivalent</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Biodiesel Quality Survey

- Samples obtained nationwide from biodiesel blenders (27 samples)
- Tested using methods in D6751 as well as stability tests
- 85% of samples tested met the ASTM D6751 specification
- Four samples failed because they exceeded limits on:
  - phosphorus
  - total glycerin
  - acid number
  - acid number and total glycerin
- Blenders/distributors depend completely on producers to insure quality
  - Only “visual” quality checks were made, no sample testing
B100 Sampling Locations

-green flags
Biodiesel Quality Survey: Sulfur

- Distributors have generally not yet begun to distinguish between S15 and S500 grades
- All but two samples met S15
- One sample exhibited 83 ppm Sulfur and 3x the allowable Phosphorus
  - Speculate lube oil contamination?
Oxidation Stability – Rancimat (EN14112)

- Air bubbled through sample at 110°C.
- Measures formation of volatile acids—not directly related to fuel performance.
- EN14214 requires min. 6 hr induction time.
- Only one US sample would meet this requirement - 6 hr induction time may not be appropriate for US biodiesel.
- Antioxidants can increase induction time.

![Oxidation Stability Graph]

**European Biodiesel Stability Standard**

<table>
<thead>
<tr>
<th>Rancimat Induction Time, hr</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16</td>
</tr>
<tr>
<td>2 - 3</td>
<td>6</td>
</tr>
<tr>
<td>3 - 4</td>
<td>2</td>
</tr>
<tr>
<td>4 - 5</td>
<td>1</td>
</tr>
<tr>
<td>5 - 6</td>
<td>1</td>
</tr>
<tr>
<td>6 - 7</td>
<td>1</td>
</tr>
</tbody>
</table>

**Test Conditions**

- Distilled Soy (D.S.)
- 500 ppm Tenox 21
- 500 ppm Pet. AO 202
- 500 ppm TBHQ
- 500 ppm Pet. AO 205
- 500 ppm BHT
- 500 ppm Pet. AO 203
- 500 ppm Pet. AO 204
- Distilled Soy (D.S.)

**Rancimat IP, 110°C, h**
Oxidation Stability – D2274

- Exposure to oxygen at 95°C for 16 hours
- Filtration and weighing of deposits – directly related to fuel performance
- Limits for this test have not been determined for biodiesel
- Antioxidants are effective for reducing deposits

Considerable work remains to determine an appropriate test and limit for biodiesel oxidation stability.
Emissions in Older Engines

- EPA analysis:
  - data from many studies
  - engine models through 1997
- NOx 2% increase B20, 10% for B100
- PM 10% decrease for B20, 50% for B100

EPA420-P-02-001, October 2002
Newer Engines: 2004 Cummins ISB – B100

HD FTP compared to ULSD
Larger NOx increase than older engines
– 31% vs 10%
More saturated fuel (tallow) has somewhat lower NOx
Large PM reduction than older engines
– 75% versus 50%
EGR valve opens less on B100 compared to ULSD
New Engines: Single-Cylinder Caterpillar Engine – B20

- 8-Mode SS compared to oil sands No. 2
- Single cylinder engine modified with EGR to meet 2004 standard.
- NOx increase larger than for older engines
  - 9% vs 2%
- PM reduction larger than for older engines
  - 25% vs 10%
New Engines: 2004 DDC Series 60 – B20

- HD FTP compared to ULSD
- Similar NOx increase as older engines
  - 3.5% vs 2%
- Larger PM reduction than older engines
  - 28% versus 10%
Why Does Biodiesel Increase NOx?

- Biodiesel exhibits higher bulk modulus of compressibility than petro-diesel
- van Gerpen proposed that this causes advance in injection timing, increasing NOx (J. Am. Oil Chemists Society, 2000. 77(3):285).
- More recently, Boehman has shown this experimentally, and that the start of combustion is also advanced by up to 4 CA degrees (SAE 2003-01-1039).
- Biodiesel NOx may increase because of advanced injection timing and start of combustion
Biodiesel PM Reduction Mechanism Revealed

Research at Sandia National Laboratories/California (Chuck Mueller)

- Approach: Use optical-engine experiments to enhance fundamental understanding of biodiesel combustion and emissions formation
  - Complemented by kinetic modeling and carbon-14 isotopic labeling collaborations with Lawrence Livermore National Lab
- Recent result: Direct formation of CO2 from ester causes two O-atoms to be used to remove one C-atom
  - Ideally, each O-atom in fuel removes one C-atom from soot-formation pathways
  - (i.e., one O-atom is wasted)
  - Ester structure found in biodiesel is less effective than ether at suppressing soot emissions
- Current focus: Determine reason(s) for elevated NOx emissions with biodiesel fueling
  - Collaboration with Prof. Ed Cheng of San Francisco State Univ.
Potential for Biodiesel in LTC Explored

Research at Oak Ridge National Laboratory (Wagner et al.)

- Biodiesel (B100) did not show a transition into high-efficiency clean combustion.
- Somewhat surprising, expected O₂ content to help.
- All three petroleum-based fuels (CERT, CARB, ECD1) behaved very similarly.
- B100 data was very erratic.
- ORNL hopes to repeat some experiments this FY to confirm earlier results.

![Graph showing PM and NOx emissions for different fuels](image.png)

Transition to Low-NOₓ, Low-PM Combustion Caused by increasing EGR to 55%, changing fuel injection

Mercedes 1.7-L engine
1500 rpm/25.9 ft-lb
Closing Remarks

• Survey results indicate that 85% of US biodiesel meets the ASTM quality standard
• Oxidation stability issues still being studied
  – Best test method not yet defined
  – Antioxidants appear to be effective
• Modern (2004) engines show NOx increase and PM reduction
  – Magnitude may be larger than in older engines
  – Cause of NOx increase and solutions to this problem are still under investigation