Deployment Issues for Biodiesel:
Fuel Quality and Emission Impacts

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Office of FreedomCAR and Vehicle Technologies
Fuels Technologies Subprogram
Non-Petroleum Based Fuels Activity
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What is biodiesel?

• Mono-alkyl esters of fatty acids (i.e. methyl or ethyl esters)

100 lb triglyceride + 10 lb alcohol = 10 lb glycerine (byproduct) + 100 lb mono-alkyl ester
soy oil methanol Biodiesel

Methyl Oleate

Methyl Linoleate

Methyl Linolenate

• Must meet the quality requirements of ASTM D6751
• Typically used as blend with petrodiesel (up to 20%)
• DOE R&D effort focused on use of biodiesel at 20% or lower
Biodiesel Attributes

- High cetane (avg. over 50)
- Ultra low sulfur (avg ~ 2 ppm)
- Blends have similar energy content per gallon
- High lubricity, even in blends as low at 1-2%
- Poorer cold flow properties with high blends
- Renewable
- Reduces HC, PM, CO in existing diesel engines
- Blends can be used with no engine modification
Biodiesel Warranty Issues

• Manufacturers warrant their products against defects in materials and workmanship

• In general use of a particular fuel should have no effect on the materials and workmanship warranty

• Use of biodiesel does not “void the warranty”, this is prohibited by the Magnuson-Moss Warranty Act

• Manufacturers are concerned that extensive use of biodiesel will result in increased numbers of warranty claims for what are actually problems caused by the fuel

Engine and vehicle manufacturers are generally comfortable with blends up to 5%

Concerns about fuel quality and stability are what is preventing approval of blending levels above 5% for most manufacturers
# Warranty Statements

While manufacturers do not warrant fuel, many have position statements and recommendations on biodiesel:

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMA</td>
<td>Up to 5% biodiesel, must meet ASTM D6751.</td>
</tr>
<tr>
<td>Caterpillar</td>
<td>Many engines approved for B100, others limited to B5. Must meet ASTM D6751.</td>
</tr>
<tr>
<td>Cummins</td>
<td>All engines approved for up to 20% biodiesel, must meet ASTM D6751 and EMA B20 specification.</td>
</tr>
<tr>
<td>Detroit Diesel</td>
<td>Approve up to 20% biodiesel. Must meet DDC specific diesel fuel specification.</td>
</tr>
<tr>
<td>Ford</td>
<td>Up to 5% biodiesel, must meet both ASTM D6751 and EN 14214.</td>
</tr>
<tr>
<td>General Motors</td>
<td>All engines approved for up to 5% biodiesel, must meet ASTM D6751.</td>
</tr>
<tr>
<td>International</td>
<td>Approve up to 20% biodiesel, must meet ASTM D6751.</td>
</tr>
<tr>
<td>John Deere</td>
<td>All engines approved for 5% biodiesel, must meet ASTM D6751.</td>
</tr>
</tbody>
</table>

**Fuel Injection Equipment:**

| Bosch              | Up to 5% biodiesel, must meet EN 14214.                                   |
| Delphi             | Up to 5% biodiesel, must meet ASTM D6751.                                |
| Stanadyne          | Up to 20% biodiesel, must meet ASTM D6751.                               |

http://www.biodiesel.org/resources/fuelfactsheets/standards_and_warranties.shtm
Why biodiesel?
Biodiesel is truly renewable

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

Petroleum diesel uses 1.2 MJ of fossil energy to produce 1 MJ of fuel product energy

\[Fossil\ energy\ ratio = 0.83\]

Biodiesel uses 0.31 MJ of fossil energy to produce 1 MJ of fuel product energy

\[B100\ Fossil\ energy\ ratio = 3.2\]

B20 reduces life cycle petroleum consumption by 19%
B20 reduces life cycle CO\textsubscript{2} emissions by 16%

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

- Current production capacity is more than 864 million annual gallons (Jan. 2007)
- Nearly 1.7 billion annual gallon additional capacity under construction or planned (Source: NBB)
Why Biodiesel?
There is enough to make a difference.

- 1.7 billion annual gallon resource
- 3.6 billion annual gallons by 2016
- Long-Term Potential: 10 billion annual gallons by 2030

- US on-road market: 40 billion annual gallons
  - Developing new feedstock sources should be a priority

Feedstock analysis from NREL/TP-510-34796, June 2004
Biodiesel Quality
Biodiesel Production Process
–Crude Products

- Fat or Vegetable Oil
- Excess Methanol
- Catalyst (caustic soda, NaOH)

Crude Biodiesel for Purification

Crude Glycerol for Sale or Purification

Methanol for Purification and Recycle
Potential Impurities in Biodiesel

- Methanol
  - Degrades some plastics and elastomers, corrosive
  - Can lower flashpoint to unsafe levels (fire safety)
- Unconverted/partly converted fat (bound glycerin)
  - Results in very poor cold flow properties, injector and in-cylinder deposits, potential engine failure
- Glycerin (free glycerin)
  - Results in injector deposits, clogged fuel filters, deposit at bottom of fuel storage tank
- Catalyst (caustic, NaOH)
  - Excessive injector, fuel pump, piston, and ring wear, filter plugging, issues with lubricant

*All are limited by ASTM D6751 specification*
Biodiesel Quality Surveys

• B100 exhibited 15% failure rate in 2004

Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004

• Showed significant problem with meeting B100 requirements in 2006
  – 50% failure rate
  – Report in preparation
  – NBB response

• Identified problems with consistent blending of B20 in 2004

• Additional surveys ongoing
  – Surveys and education needed on a continuous basis
Buying Quality Biodiesel – B100

• Demand that the supplier provide a certificate of analysis showing compliance with D6751 for every batch of biodiesel they produce
  – This is the basic requirement of the BQ-9000 program
  – If the supplier cannot provide this, find a different supplier
Biodiesel Degradation

• Microbial contamination
  – Biodiesel is biodegradable
  – Microbes form films or mats that can plug filters
  – Requires water in storage tank
  – Storage tank housekeeping issue/biocide treatment
  – Also an issue for petroleum fuels

• Oxidation
  – Increases acidity (limited in D6751 to 0.5)
  – Forms gums
  – A stability requirement is included in D6751
Biodiesel Stability

- NREL/NBB stability study shows that blend stability is dominated by B100 stability
- This work led directly to the adoption of a stability requirement for B100 by ASTM
  - 3 hour OSI induction time
  - Final report in preparation

“Cummins is able to upgrade its previous position on the use of biodiesel fuel, which limited the use to B5 blends only, up to B20 for three key reasons. First, the American Society of Testing Materials specification ASTM D6751 now includes an important stability specification for B100 biodiesel.”

Empirical Study of the Stability of Biodiesel and Biodiesel Blends
http://www.nrel.gov/docs/fy07osti/41619.pdf
Emissions
Emission Impact of B20

- 10% to 25% reduction in PM and CO, depending on engine, test cycle, and other factors
- 5% to 15% reduction on total HC and toxic compounds including: Aldehydes, PAH, NPAH
- Impact on NO\textsubscript{x} emissions less certain
  - EPA review of published data found B20 causing NO\textsubscript{x} to go up ~2%
  - But many studies show NO\textsubscript{x} going down
Biodiesel’s Effect on NO\textsubscript{x} Emissions

EPA Review - Engine Data

- Percent change in NO\textsubscript{x} for B20 ranges from -7% to +7%
- Average change in NO\textsubscript{x} +2% *(EPA’s conclusion)*

Many B20 tests show NO\textsubscript{x} decreasing:
- All are for soy biodiesel
- Engine standards groups D and E

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### EPA Report

<table>
<thead>
<tr>
<th>Standards group</th>
<th>Model years</th>
<th>HD highway engines</th>
<th>NOx observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>2002 - 2006</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>1998 - 2001</td>
<td>2</td>
<td>14 (2)*</td>
</tr>
<tr>
<td>D</td>
<td>1994 - 1997</td>
<td>10</td>
<td>152 (19)</td>
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<tr>
<td>E</td>
<td>1991 - 1993</td>
<td>16</td>
<td>394 (50)</td>
</tr>
<tr>
<td>F</td>
<td>1990</td>
<td>3</td>
<td>87 (11)</td>
</tr>
<tr>
<td>G</td>
<td>1988 - 1989</td>
<td>8</td>
<td>112 (14)</td>
</tr>
<tr>
<td>H</td>
<td>1984 - 1987</td>
<td>2</td>
<td>16 (2)</td>
</tr>
<tr>
<td>I</td>
<td>- 1983</td>
<td>2</td>
<td>10 (1)</td>
</tr>
</tbody>
</table>

* Values in parentheses are percent of total observations

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EPA420-P-02-001, Draft Report, October 2002
EPA Review – Engine Data

- 43 engines included
- 785 total observations
- 72% of engines pre-1994
- 95% pre-1997
- 45% is 1991 DDC Series 60 (shows consistent small NOx increase)
**NREL Vehicle Testing Study**

- Percent change in NO\(_x\) ranges from -5.8% to +6.2%
- *Average change in NO\(_x\) is 0.6% ±1.8%*
- Because of variability, conclusion may not apply to all in-use vehicles

<table>
<thead>
<tr>
<th>Vehicle</th>
<th>Cycle</th>
<th>NO(_x)</th>
<th>PM</th>
<th>CO</th>
<th>THC</th>
<th>Fuel Economy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transit Bus #1</td>
<td>CSHVC</td>
<td>-5.8</td>
<td>-17</td>
<td>-27</td>
<td>-28</td>
<td>-2.2</td>
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<tr>
<td>Transit Bus #2</td>
<td>CSHVC</td>
<td>-3.9</td>
<td>-33</td>
<td>-20</td>
<td>-28</td>
<td>-2</td>
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<tr>
<td>Transit Bus #3 (avg both)</td>
<td>CSHVC</td>
<td>-3.2</td>
<td>-19</td>
<td>-15</td>
<td>-24</td>
<td>-1.9</td>
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<td>Freightliner Class 8</td>
<td>CSHVC</td>
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<td>-15</td>
<td>-1.5</td>
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<td></td>
<td>Freeway</td>
<td>3.6</td>
<td>-26</td>
<td>-7</td>
<td>-16</td>
<td>-1.6</td>
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<td>Motor Coach</td>
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<td>-22</td>
<td>-15</td>
<td>-1.3</td>
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<td></td>
<td>UDDS</td>
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<td>-19</td>
<td>-3</td>
<td>-0.6</td>
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<td>International Class 8</td>
<td>CILCCmod</td>
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<td>-15</td>
<td>-17</td>
<td>-2.3</td>
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<tr>
<td></td>
<td>Freeway</td>
<td>2.3</td>
<td>-35</td>
<td>-15</td>
<td>-12</td>
<td>-0.5</td>
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<tr>
<td>Green Diesel School Bus</td>
<td>CSHVC</td>
<td>-0.8</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>-2</td>
</tr>
<tr>
<td></td>
<td>RU CSCBC</td>
<td>2.3</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>-0.8</td>
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<td>Conventional School Bus</td>
<td>CSHVC</td>
<td>-0.7</td>
<td>3</td>
<td>10</td>
<td>-1</td>
<td>-1.1</td>
</tr>
<tr>
<td></td>
<td>RU CSCBC</td>
<td>6.2</td>
<td>-24</td>
<td>-23</td>
<td>-20</td>
<td>-0.3</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.6</td>
<td>-23</td>
<td>-15</td>
<td>-16</td>
<td>-1.4</td>
</tr>
<tr>
<td>95%+/-</td>
<td>1.8</td>
<td>10.2</td>
<td>6.1</td>
<td>8.6</td>
<td>0.4</td>
<td></td>
</tr>
</tbody>
</table>

*Vehicle equipped with diesel particle filter, changes in PM, CO, and THC not statistically significant*

**Effects of Biodiesel Blends on Vehicle Emissions:**
http://www.nrel.gov/docs/fy07osti/40554.pdf
Summary – Biodiesel NO\textsubscript{x} Impact

- NO\textsubscript{x} can increase or decrease depending on engine
- Data compilations that are not weighted to one engine model show no change in NO\textsubscript{x} on average for B20
- Additional research is needed to quantify impact
- Reduction in PM, CO, and THC is robust

These results have led EPA to make a more neutral statement about biodiesel’s NO\textsubscript{x} impact (RFS Final Rule):
  - Conclusion that NO\textsubscript{x} increases not widely accepted
  - Conflicting results from other studies
  - Additional studies involving all stakeholders are planned

Effects of Biodiesel Blends on Vehicle Emissions:
http://www.nrel.gov/docs/fy07osti/40554.pdf
B20 Testing with DPF – HD FTP

B20 results in substantial PM reduction even with DPF (data for 2003 Cummins ISB with Johnson Matthey CCRT on HD FTP)

Reduction with DPF ranges from 20% to 70%, depending on basefuel, test cycle, and other factors:
- Reduction in sulfate emissions
- Increased PM reactivity

Williams, et al., “Effect of Biodiesel Blends on Diesel Particulate Filter Performance” SAE 2006-01-3280
Closing Remarks

• Biodiesel is a significant sustainable energy resource for the United States
• Use of high quality biodiesel meeting ASTM D6751 (or other national standard) is critical for good performance
• Development of new feedstock sources (energy crops, algae, etc.) is critical for the development of this industry
• B20 produces robust reductions in emissions of soot, toxics, and carbon monoxide
• B20 appears to have no consistent impact on emissions of NOx

http://www.nrel.gov/vehiclesandfuels(npbf/pubs_biodiesel.html}