Biodiesel Utilization: Update on Analytical Techniques

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Key Points of Biodiesel Utilization

- 2007: Energy Independence and Security Act mandates biodiesel production in the United States starting with 500M gallons in 2009, increasing to 1B gallons in 2012¹
  - Diesel sales are 63B gallons in 2007²
- 2008: 700M gallons of biodiesel produced in United States³
- October 2008: ASTM adopted Bxx blend specifications
- March 2009: EU added tariff on imported biodiesel⁴
- Therefore, biodiesel is being used in the United States

Topics for Discussion

• Biodiesel in lubrication oil
• Cold soak filtration
Biodiesel in Lubrication Oil

• Biodiesel is less volatile than diesel fuel
  • Possible accumulation in lubrication oil
• Traditional GC methods for fuel dilution don’t account for biodiesel (ASTM D3524)
• FTIR/ATR method (D7371) for biodiesel in diesel fuel may be modified to detect biodiesel in lube oil
  • Strong C=O stretch between 1750 cm\(^{-1}\) to 1650 cm\(^{-1}\)
• How does lube oil base stock impact results?
Benefits of FTIR/ATR

- Horizontal ZnSe 45° multi-bounce ATR cell
- Short path length (10-20 \(\mu\)m) allows measurement of used lubrication oil (soot readily absorbs IR)
- Cell maintains fixed path length over useful life
- Rapid analysis time (~60 seconds) for 32 scans and 4 cm\(^{-1}\) resolution
Engine Durability Tests

- Run diesel engine over durability cycle with advanced emission control systems – NAC and SCR
  - Late cylinder injection and/or fuel injection into exhaust for emission control
- Oil was changed at recommended intervals
  - Collect aliquot for fuel dilution analysis
- Validate FTIR/ATR technique to quantify biodiesel dilution in lube oil
  - PLS model built with fresh oil from project and typical soy-derived biodiesel
    - Base stock character can impact quantitation results

NAC = NOx adsorber catalyst
SCR = selective catalytic reduction
# Engine and Fuel

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine Power</td>
<td>113 kW at 4,000 rpm</td>
</tr>
<tr>
<td>Peak Torque</td>
<td>360 Nm at 2,000 rpm</td>
</tr>
<tr>
<td>Max. Engine Speed</td>
<td>4,700 rpm</td>
</tr>
<tr>
<td>Max. BMEP</td>
<td>21 bar</td>
</tr>
<tr>
<td>Cylinder/Firing Order</td>
<td>I-4, 1-3-4-2</td>
</tr>
<tr>
<td>Bore to Stroke Ratio</td>
<td>1.0034</td>
</tr>
<tr>
<td>Displacement</td>
<td>2.15 L</td>
</tr>
<tr>
<td>Compression Ratio</td>
<td>18:1</td>
</tr>
<tr>
<td>Fuel Injection System</td>
<td>2nd Generation Common Rail</td>
</tr>
<tr>
<td>Fuel</td>
<td>Soybean-derived B20</td>
</tr>
</tbody>
</table>

Source: SAE 2009-01-1790
# Emission Control System Parameters

<table>
<thead>
<tr>
<th>System</th>
<th>Component</th>
<th>Vol. (L)</th>
<th>Cell Density (cpsi)</th>
<th>PGM Loading (g/ft³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAC system</td>
<td>DOC</td>
<td>0.8</td>
<td>400</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>DPF</td>
<td>3.3</td>
<td>300</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>NAC</td>
<td>4.1</td>
<td>400</td>
<td>120</td>
</tr>
<tr>
<td>SCR system</td>
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<td>150</td>
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<tr>
<td></td>
<td>DPF</td>
<td>4.1</td>
<td>300</td>
<td>60</td>
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<tr>
<td></td>
<td>SCR FeZSM-5</td>
<td>4.43</td>
<td>300</td>
<td>NA</td>
</tr>
</tbody>
</table>

Source: SAE 2009-01-1790
Differences in Base Oil

- Note the differences between 1800 cm\(^{-1}\) and 1700 cm\(^{-1}\) (carbonyl stretch \(~1750\) cm\(^{-1}\) )
- These differences can lead to over/underreporting of biodiesel dilution
“Good” vs. “Bad” Calibration Model

- Same sample quantified with parent and unrelated base oil
- Dissimilar base oil leads to underestimation of biodiesel dilution (blue/purple curves)
- Red curve is correct $\rightarrow$ 6.5 vol% biodiesel
Another Example

- Valid result (red) is 7.0 vol% dilution; invalid result (blue/purple) is ~50% low
## Results

### NAC

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Oil Age (hrs)</th>
<th>System Age (hrs)</th>
<th>Biodiesel (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48</td>
<td>48</td>
<td>4.7</td>
</tr>
<tr>
<td>2</td>
<td>92</td>
<td>140</td>
<td>6.6</td>
</tr>
<tr>
<td>3</td>
<td>65</td>
<td>205</td>
<td>5.2</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>295</td>
<td>5.7</td>
</tr>
<tr>
<td>5</td>
<td>67</td>
<td>362</td>
<td>5.3</td>
</tr>
<tr>
<td>6</td>
<td>65</td>
<td>427</td>
<td>6.8</td>
</tr>
<tr>
<td>7</td>
<td>65</td>
<td>492</td>
<td>5.9</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>592</td>
<td>8.3</td>
</tr>
<tr>
<td>9</td>
<td>158</td>
<td>750</td>
<td>10.1</td>
</tr>
</tbody>
</table>

### SCR

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Oil Age (hrs)</th>
<th>System Age (hrs)</th>
<th>Biodiesel (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65</td>
<td>65</td>
<td>8.0</td>
</tr>
<tr>
<td>2</td>
<td>76</td>
<td>141</td>
<td>7.6</td>
</tr>
<tr>
<td>3</td>
<td>54</td>
<td>195</td>
<td>6.5</td>
</tr>
<tr>
<td>4</td>
<td>65</td>
<td>260</td>
<td>7.0</td>
</tr>
<tr>
<td>5</td>
<td>59</td>
<td>319</td>
<td>4.1</td>
</tr>
<tr>
<td>6</td>
<td>63</td>
<td>382</td>
<td>4.7</td>
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<tr>
<td>7</td>
<td>58</td>
<td>440</td>
<td>4.1</td>
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<tr>
<td>8</td>
<td>64</td>
<td>504</td>
<td>3.7</td>
</tr>
<tr>
<td>9</td>
<td>64</td>
<td>568</td>
<td>3.6</td>
</tr>
<tr>
<td>10</td>
<td>45</td>
<td>613</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Diesel dilution tracks biodiesel dilution, but is typically 50%-67% lower.
Additional Lubricant Results

- Each oil change represents ~10,000 mi
- TBN decrease is due to normal lubricant aging
- TBN and TAN never cross
  - Lubricant is within normal service interval

TBN = total base number
TAN = total acid number
Wrap-up

- FTIR/ATR is a robust analytical technique to quantify biodiesel dilution in lubrication oil
- It is critical to use the same base oil for calibration that is used in testing
  - Poorly designed model can lead to over/underestimation
- Future research should examine a single technique to quantify biodiesel and diesel in lubrication oil, especially if base stock is unknown
Cold Soak Filtration Analysis

- Some biodiesel samples exhibit precipitates above the cloud point
  - Cold soak filtration test (CSFT) was adopted as performance specification in ASTM D6751 in October 2008
- CSFT results are bimodal, either passing (<360 second filtration time) or failing (>720 second filtration time)
CSFT Method

- B100 is chilled to 4.5°C for 16 hours, then warmed and vacuum filtered through 0.7 μm filter; filtration time is reported
- Intent was to make Annex method “official”
- Annex method was used as a starting point to develop ASTM D7501
  - D7501 was published May 2009
Comparison of CSFT Annex to D7501

**CSFT Annex**
- Sample can be cooled in lunchroom fridge
- Warm sample on bench top
  - Time to warm may vary greatly
- Filter selection is overly broad

**D7501 CSFT**
- Tighter control of chilling apparatus
- Warm sample in 25°C circulating liquid bath
  - Warm time is specified
- Specific filter brand/type
Impact of Filter Type on CSFT

- Filter A
- Filter B
- Filter C
- Filter D

Graph showing the relationship between filtration time in seconds for different filters using Annex and D7501 Methods.
Filter Differences

- Data was validated in a single lab, all data is average of duplicate runs
- For most fuels, differences between filters are nominal
  - Some fuels show significant variability
- Annex method was developed on Filter A
  - Wide variety of filters available led to poor repeatability
  - In round robin testing, specification of filter in D7501 method led to better repeatability
- Annex method has reduced cold weather problems
  - Still no fundamental understanding of the root cause
Experimental Design to Determine Root Cause of Filter Plugging

• Cause of precipitates and failing filtration times are not well understood
• Potential compounds have similar character as FAME
  • Separation becomes limiting step to analysis
• Goal was to develop high-throughput technique to analyze precipitates inside the biodiesel matrix
• Previous work in lipid-based chemotaxonomic studies of bacteria shows that matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS), with an optimized matrix system, is effective in analyzing diacyl-phosphatidylethanolamines and diacyl-phosphatidylglycerols\(^1\)
• Can biodiesel precipitates be fingerprinted in the same fashion?

MALDI-TOF Background

MALDI ionization

TOF Mass analyzer

Detector

% Intensity

m/z
MALDI-TOF Background

MALDI ionization

TOF Mass analyzer

Detector

MALDI-TOF Background diagram with a multi-peak spectrum graph showing mass/charge (m/z) versus percentage intensity.
MALDI-TOF Background

MALDI ionization → TOF Mass analyzer → Detector

Graph shows % intensity vs. m/z.
Mass Analysis TOF

- Ions are analyzed by the amount of time taken to reach detector\(^1\)

- Potential energy assumed to be converted to kinetic:
  \[ \text{Ep} = \text{Ek} \]
  \[ \text{Ep} = z\text{Vo} \]
  \[ \text{Ek} = \frac{1}{2}mv^2 \]
  \[ z\text{Vo} = \frac{1}{2}mv^2 \]

- Ions of lower mass have higher velocity
- Potential can be positive or negative

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Methodology

• Take a stepwise approach
• Identify individual trace compounds thought to be present in biodiesel
• Use traditional matrix systems to evaluate pure components
• Test combinations of matrix systems to determine system over the range of components
• Utilize MS² for positive peak identification
Single Component Results

Monostearin

Distearin

Triolein

Stigmasterol

m/z = 358.56

m/z = 625.02

m/z = 885.43

m/z = 412.69
Complex Mixture Results

1) [monopalm+Na]+  
2) [dilinolein+Na]+  
3) [monoolein+Na]+  
4) [disterin+Na]+  
5) [triolein+Na]+  
6) [stigmasterol+Na]+  
7) [S.G.+Na]+
Comparison of Different Biodiesels

- Distilled Palm B100
- Mid-glycerin Palm B100
- High-glycerin Palm B100
Source: Poster to be presented at ASMS Meeting, June 1-3, 2009
Closing Thoughts

• While biodiesel is mostly FAME, industry is concerned that trace components can impact operability significantly
• To fully understand the utilization of biodiesel, careful attention needs to be paid to the analytical methodology
• Methods need to be shared and compared to ensure that accurate data is gathered for this increasingly complex fuel