Impact of Biodiesel on Ash Emissions and Lubricant Properties Affecting Fuel Economy and Engine Wear

Comparison with Conventional Diesel Fuel

August 15, 2007

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Fuel and lubricant composition affects engine and aftertreatment system (ATS) performance.

**Motivation**

- **Fuel Dilution**
  - ATS requirements
  - Fuel properties

- **Consequences**
  - Physical - Viscometric properties
  - Chemical - Interfere with additive performance

**Fuel**
- Bio-Fuels
- Petroleum

**Bio-Fuels**
- Na, K, Ca, Mg - ash
- P – catalyst deactivation

**Petroleum Fuels**
- S – catalyst deactivation

**Effect of bio-fuel on lubricant properties via fuel dilution and ATS performance via PM and ash emissions not well known.**
Background

- **Bio-fuel effects on aftertreatment system (ATS) performance**
  - Potential for residual alkali and alkaline earth metals to form ash
    - ASTM D6751 – 5 ppm limits for Na and K, Ca and Mg
    - 1 ppm\(_w\) trace metal in fuel \(\sim 22\) g trace metal in DPF per 100k miles assuming 15 mpg and 100% trapping efficiency
  - Decreased PM emissions
    - Reduce frequency of regeneration
    - Bio-diesel generated PM may oxidize more rapidly

- **Bio-fuel effects on lubricant properties**
  - Distillation characteristics and boiling range affect amount of fuel reaches cylinder walls*
  - Initial decrease followed by increase in lubricant viscosity due to oxidation and polymerization of fuel constituents (SAE 2005-26-356)
  - Polar nature of methyl esters may react with P in ZDDP to form complexes preventing anti-wear additives from coating surfaces (SAE 2006-01-3301)
  - Polar species may destabilize over-based detergents (SAE 2003-01-3140)
Experimental Apparatus

- **Cummins ISB 300**
  - Variable geometry turbocharger
  - Cooled EGR
  - Common rail fuel injection
  - Fully electronically controlled

- **PM Sampling**
  - Conventional 47 mm filters
  - Individual particulate collection using 3mm dia. TEM grids

- **Sample Analysis**
  - Horiba MEXA 1370 – SOL, SOF, SO$_4$
  - TGA – Total ash content
  - Scanning Transmission Electron Microscopy (STEM)
    - PM and ash morphology and elemental composition

Comparison of conventional 47mm filters and 3mm sample grids
Accelerated Fuel Dilution System

**Objective:** Simulate fuel dilution and accelerate lubricant aging under controlled conditions.

**Key Parameters**
- **Temperature:** 165 °C sump, 220 °C inlet
- **Volume:** 1 L lubricant (6 L max.)
- **Speed:** 5.5 rpm (30 max.)
- **Duration:** 12 hrs steady state

**Test Matrix**
- CI-4, CJ-4 oil
- No dilution
- 5% ULSD, 5% SME B100

**Test Sequence**
1. Rapid aging system: 12 hours
2. Bench oxidation: 78 hours

**Lubricant Analysis**
- TAN, TBN, Viscosity, FTIR, ICP
- 4-Ball Wear
### Lubricant Elemental Analysis

<table>
<thead>
<tr>
<th>Lubricant Condition</th>
<th>B (ppm)</th>
<th>Ca (ppm)</th>
<th>Fe (ppm)</th>
<th>Mg (ppm)</th>
<th>Mo (ppm)</th>
<th>P (ppm)</th>
<th>Zn (ppm)</th>
<th>S (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh CI-4</td>
<td>&lt;1</td>
<td>2352</td>
<td>2</td>
<td>269</td>
<td>1</td>
<td>1181</td>
<td>1398</td>
<td>5863</td>
</tr>
<tr>
<td>Fresh CJ-4</td>
<td>586</td>
<td>1388</td>
<td>2</td>
<td>355</td>
<td>77</td>
<td>985</td>
<td>1226</td>
<td>4606</td>
</tr>
<tr>
<td>Engine Aged CI-4</td>
<td>18</td>
<td>2626</td>
<td>20</td>
<td>267</td>
<td>11</td>
<td>1246</td>
<td>1464</td>
<td>6076</td>
</tr>
</tbody>
</table>

Lubricant run in engine for approximately 220 hours at time of sampling

### Lubricant Properties

<table>
<thead>
<tr>
<th>Lubricant Condition</th>
<th>ASTM D3524 Fuel [% Wt]</th>
<th>ASTM D3524 Soot [% Wt]</th>
<th>ASTM D3524 Water [% Vol]</th>
<th>ASTM D445 Visc. @100 C [mm²/s]</th>
<th>ASTM D664 TAN [mg KOH/g]</th>
<th>ASTM D2896 TBN [mg KOH/g]</th>
<th>ASTM D4739 TBN [mg KOH/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh CI-4</td>
<td>&lt;0.1%</td>
<td>&lt;0.1%</td>
<td>&lt;0.1%</td>
<td>14.93</td>
<td>1.86</td>
<td>9.94</td>
<td>---</td>
</tr>
<tr>
<td>Fresh CJ-4</td>
<td>&lt;0.1%</td>
<td>&lt;0.1%</td>
<td>&lt;0.1%</td>
<td>15.8</td>
<td>1.74</td>
<td>9.6*</td>
<td>6.66</td>
</tr>
<tr>
<td>Engine Aged CI-4</td>
<td>&lt;0.1%</td>
<td>0.10%</td>
<td>&lt;0.1%</td>
<td>13.13</td>
<td>2.17</td>
<td>10.42</td>
<td>---</td>
</tr>
</tbody>
</table>

* Supplied by manufacturer

New and engine aged lubricant provide reference for comparison to accelerated test results
### Fuel Properties and Hardware Compatibility

**Trace element levels in commercial B100 SME**

<table>
<thead>
<tr>
<th>Element</th>
<th>ASTM D5185</th>
<th></th>
<th>B100 Batch 1</th>
<th>B100 Used</th>
<th>B100 Batch 2</th>
<th>ULSD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lowest</td>
<td>B100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reporting</td>
<td>[ppb]</td>
<td>[ppb]</td>
<td>[ppb]</td>
<td>[ppb]</td>
<td>[ppb]</td>
</tr>
<tr>
<td>Calcium, Ca</td>
<td>[ppb]</td>
<td>97</td>
<td>410</td>
<td>198</td>
<td>140</td>
<td>&lt;97</td>
</tr>
<tr>
<td>Magnesium, Mg</td>
<td>[ppb]</td>
<td>56</td>
<td>&lt;56</td>
<td>&lt;56</td>
<td>&lt;56</td>
<td>&lt;56</td>
</tr>
<tr>
<td>Phosphorus, P</td>
<td>[ppb]</td>
<td>1,180</td>
<td>&lt;1180</td>
<td>2981</td>
<td>&lt;1180</td>
<td>&lt;1180</td>
</tr>
<tr>
<td>Sodium, Na</td>
<td>[ppb]</td>
<td>2,010</td>
<td>&lt;2010</td>
<td>22587</td>
<td>&lt;2010</td>
<td>&lt;2010</td>
</tr>
<tr>
<td>Potassium, K</td>
<td>[ppb]</td>
<td>2,690</td>
<td>&lt;2690</td>
<td>&lt;2690</td>
<td>&lt;2690</td>
<td>&lt;2690</td>
</tr>
<tr>
<td>Zinc, Zn</td>
<td>[ppb]</td>
<td>155</td>
<td>&lt;155</td>
<td>&lt;155</td>
<td>&lt;155</td>
<td>&lt;155</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ASTM D664</th>
<th>ASTM D3828</th>
<th>ASTM D6304</th>
<th>EN 14112</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Number</td>
<td>Flash Point*</td>
<td>Water</td>
<td>Rancimat</td>
</tr>
<tr>
<td>[mg KOH/g]</td>
<td>[ °C]</td>
<td>[ppm]</td>
<td>[hr]</td>
</tr>
<tr>
<td>B100 - Batch 1</td>
<td>0.23</td>
<td>&gt;130</td>
<td>314</td>
</tr>
<tr>
<td>B100 - Used</td>
<td>3.36</td>
<td>&lt;130</td>
<td>499</td>
</tr>
<tr>
<td>ASTM D6751</td>
<td>0.5 max</td>
<td>130 min</td>
<td>500 max</td>
</tr>
</tbody>
</table>

Injector failure after short duration use with low quality B100 shown in tables as (B100-Used)
B100 SME shows 70% reduction in PM

- Increase in NOx/PM ratio ~ 3X
- Reduced soot loading of engine lubricant
- Aside from soot no additional differences in B100 combustion products observed to affect lubricant

### NOx/PM NO₂/NOx

<table>
<thead>
<tr>
<th></th>
<th>NOx/PM</th>
<th>NO₂/NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULSD</td>
<td>12.8</td>
<td>0.055</td>
</tr>
<tr>
<td>B100</td>
<td>43.8</td>
<td>0.044</td>
</tr>
</tbody>
</table>

### Total soot in lubricant

<table>
<thead>
<tr>
<th>Total soot in lubricant</th>
<th>Soot [% Wt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Oil: CI-4</td>
<td>&lt;0.1%</td>
</tr>
<tr>
<td>Engine Aged ULSD</td>
<td>0.10%</td>
</tr>
<tr>
<td>Rapid Aged ULSD</td>
<td>0.10%</td>
</tr>
<tr>
<td>Rapid Aged B100</td>
<td>&lt;0.1%</td>
</tr>
</tbody>
</table>
Potential for Increased Ash and Faster PM Oxidation

Typical PM TGA Analysis

- **Ash Fraction**
  - 1682 rpm, 25% load
  - B100: 1.85% of TPM
  - ULSD: 0.44% of TPM

- **Adjusted Ash Emissions**
  - Account for PM reduction
  - Net Increase in ash with B100 approx. **21.7%**

Biodiesel PM contains more $O_2$ - may increase soot oxidation rate
Biodiesel Ash Shows Increased Debris and Metals

Elevated levels of trace metals in biodiesel ash possibly due to solvent properties of fuel
Elevated levels of Cu and trace metals found in B100 PM

Cu particles observed in B100 ash as well

Only trace amounts of Fe typically observed in ULSD PM
Fuel Dilution Effects on Lubricant Properties

- TBN, TAN [mg KOH/g]
- Viscosity @100 °C [mm²/s]

CJ-4 Oil
Test: 12 hr rapid aged
Condition: 165 °C sump, 220 °C inlet

Test: 78 hr bench oxidation
Condition: 170 °C, 13 L/h air

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**TBN ASTM D4739, TAN ASTM D664**
- Fuel dilution at 5% shows reduced TBN decline and TAN increase
- Biodiesel most significant effect on reducing TAN and TBN change

**Viscosity ASTM D445**
- Viscosity trends follow observed TAN increase
- Effect of 12 hr rapid aging system on viscosity and TAN increase most significant
Biodiesel ester peak can interfere with lubricant oxidation measurements
Oxidation Characteristics

CJ-4 Oil Test: 12 hr rapid aged
Test: 78 hr bench oxidation
Condition: 165 °C sump, 220 °C inlet

CJ-4 Oil Test: 12 hr rapid aged
Condition: 170 °C, 13 L/h air

- Apparent increase in oxidation in biodiesel fuel dilution case due to ester interference in oxidation (carbonyl) range
- Ester peak disappears following high temperature degradation test indicating B100 loss
- Acid carbonyl (1690-1720 cm\(^{-1}\)) increases over duration of test
- No significant difference in oxidation characteristics of lubricant subject to 5% B100 fuel dilution
Biodiesel Interactions with Anti-Wear Additives

ZDDP Functionality
- Decreases with increasing ester content in lubricant
- Small dilution effect accounted for with ULSD
- Quantification extremely sensitive to integration range

4-Ball Wear - ASTM D4172

Wear Test
- 5% ULSD & B100 in CJ-4
- No significant difference between ULSD and B100 fuel dilution
- Largest effect due to physical dilution of oil independent of fuel
Conclusions (1)

B100 Impact on Emission Aftertreatment Systems

- Reduced PM emissions increase favorable NOx/PM ratio and may reduce DPF regeneration frequency with possible fuel economy benefits
- Potential for trace metals and P in biodiesel below ASTM D6751 mandated level may impact ash loading and catalyst performance
- Increase in ash emissions with B100 SME due to metal debris primarily attributed to solvent properties of fuel
- Elevated levels of metal debris in B100 PM expected to decrease over time with use of B100 in system
Conclusions (2)

B100 Lubricant Fuel Dilution Effects

- Apparent increased oxidation levels of lubricant with B100 fuel dilution attributed to B100 ester peak and not actual lubricant degradation
- Magnitude of biodiesel ester carbonyl interference measurements depends on fuel quality
- Potential for biodiesel ZDDP interaction as evidenced by decrease in ZDDP functionality in FTIR spectra
- Wear tests show no difference in B100 vs. ULSD fuel dilution at 5% fuel dilution levels

Effects of B100 on lubricant properties and aftertreatment system highly dependent on specific fuel type and composition

Short duration use of poor quality fuels can have serious consequences
Acknowledgements

- Research supported by: MIT Consortium to Optimize Lubricant and Diesel Engines for Robust Emission Aftertreatment Systems
- We thank the following organizations for their support

  Cummins       Caterpillar       Komatsu
  Ford          Chevron          Valvoline
  Süd-Chemie    Lutek            U.S. DOE/ORNL
  Ciba Specialty Chemicals

- MIT Center for Materials Science and Engineering
Questions...