Biodiesel and Renewable Diesel Emissions Study
VOC, Carbonyl & N$_2$O Emissions

Christopher Brandow
Dec 8, 2010
Acknowledgements

MLD Southern Branch
Organic Analysis

Richard Ong
Michael Okafor
Yong Yu
Lyman Dinkins
Christine Maddox
Richard Ling
Paul Rieger
## Engines and Fuels

<table>
<thead>
<tr>
<th>Make/model/year</th>
<th>Emission Control Devices</th>
<th>Test fuels</th>
<th>Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000 Freightliner C15 Caterpillar</td>
<td>ULSD diesel, Soy-based biodiesel (S20, S50, S100), Animal-based (A20, A50, A100), Renewable diesel (R20, R50, R100)</td>
<td>VOC Carbonyl N2O</td>
<td></td>
</tr>
<tr>
<td>2006 International ISM 370</td>
<td>ULSD diesel, Soy-based biodiesel (S20, S50, S100), Animal-based (A20, A50, A100),</td>
<td>VOC Carbonyl</td>
<td></td>
</tr>
<tr>
<td>2008 Freightliner Mercedes Benz MBE 4000</td>
<td>ULSD diesel, Soy-based biodiesel (S20, S50, S100), Animal-based (A20, A50, A100),</td>
<td>VOC Carbonyl</td>
<td></td>
</tr>
</tbody>
</table>
Emissions Analyses

- Speciated non-methane hydrocarbons (NMHC)
- Carbonyl compounds
- Nitrous Oxide (N2O)
# Instrumentation

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Sample Container</th>
<th>Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMHC</td>
<td>Tedlar Bag</td>
<td>Gas Chromatograph (GC) with flame ionization detector (FID)</td>
</tr>
<tr>
<td>Carbonyls</td>
<td>DNPH* Cartridge</td>
<td>High performance liquid chromatograph (HPLC) with UV detector</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}$</td>
<td>Tedlar Bag</td>
<td>Fourier transform infrared spectrometer (FTIR)</td>
</tr>
</tbody>
</table>

* Sampling cartridge impregnated with 2,4-dinitrophenylhydrazine
Speciated Non-Methane Hydrocarbon Analysis

- Tedlar bag samples analyzed by 2 GC/FIDs, connected in parallel
  - Light-end GC: C1 to C5 HCs
  - Mid-range GC: C6 to C12 HCs
- Liquid nitrogen trapping of sample yields FID detection limits to very low ppbC
Speciated Non-Methane Hydrocarbon Analysis

- Compounds reported for this study:

  1,3-butadiene
  benzene
  toluene
  ethylbenzene
  m-/p-xylene
  styrene
  o-xylene
Toxic VOC - ULSD
Toxic VOC - Soy Biodiesel
Toxic VOC - Animal Biodiesel

ULSD Benzene

Bar chart showing the levels of various VOCs in different biodiesel blends and test conditions.
Toxic VOC - C15

UDDS

Cruise
NITROUS OXIDE ANALYSIS

- Tedlar bag samples analyzed by Fourier transform infrared spectroscopy (FTIR)
  - 10-Meter, folded path IR cell
N$_2$O – C15 Engine
Carbonyl Analysis (Aldehydes and Ketones)

- Carbonyl group derivatized by DNPH in sampling cartridge*
- Cartridges flushed with solvent to extract carbonyl compounds
- Solution analyzed by high performance liquid chromatograph (HPLC) with UV detection
Carbonyl Analysis
(Aldehydes and Ketones)

• This method measures:
  – formaldehyde
  – acetaldehyde
  – acrolein*
  – 10 Other carbonyls (to C₆)
Carbonyl - ULSD
Carbonyl - Soy Biodiesel

ULSD Carbonyl Sum

Formaldehyde
Acetaldehyde
Acrolein
Sum

mL/mile

$S20$ $S50$ $S100$ $S20$ $S50$ $S100$ $S20$ $S50$ $S100$ $S20$ $S50$ $S100$ $S20$ $S50$ $S100$

C15
ISM
MBE4000
C15
ISM
MBE4000

UDDS
Cruise-50
Carbonyl - Animal Biodiesel
Carbonyl-MBE4000

UDDS

Cruise
Summary - VOC

• Soy Biodiesel
  – No significant VOC increase versus ULSD Fuel
  – No trend with regard to increasing Biodiesel fractions

• Animal Biodiesel
  – Modest VOC decrease versus ULSD Fuel
  – VOC reduced with increasing Biodiesel fractions

• Renewable Biodiesel
  – Modest VOC decrease in UDDS cycle versus ULSD fuel but not in cruise
  – VOC reduced with increasing Biodiesel fraction in UDDS but not in cruise
• No significant change in N2O emissions is observed for any fuel blend
Summary - Carbonyl

• Soy Biodiesel
  – No significant changes versus ULSD Fuel
  – No trend with regards to increasing Biodiesel fractions

• Animal Biodiesel
  – Modest decrease versus USLD Fuel in UDDS Cycle only
  – emissions reduced with increasing Biodiesel fractions.

• Renewable Biodiesel
  – No significant changes versus ULSD
Summary - Engines

- **VOC**
  - C15 and ISM engines perform similarly to each other under all fuel scenarios
  - MBE4000 emits $\sim <1/10^{th}$ of the average of C15 and ISM engines

- **Carbonyls**
  - C15 and ISM engines perform similarly to each other under all fuel scenarios
  - MBE4000 emits $\sim <1/6^{th}$ of the average of C15 and ISM engines