Impact of Copper on Fuels

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Background: Copper and fuel

• Well known that exposure to copper can accelerate fuel degradation in lab tests
• Example – Dunn and Sauer reported in 1958 on a test to evaluate the yellow metal sensitivity of different petroleum fuels
• Example – NORA Guide to Fuel Performance, 2004 noted copper lines should be avoided with petroleum fuels

HOWEVER – Copper lines are widely used in home oil heating systems and have been for many decades.
Objectives

• With increased use of Biodiesel, the Oxidative Reserve (Rancimat) test is being used increasingly to evaluate fuel against the ASTM D396 specifications.
  • Can exposure to copper in the fuel lines affect the results of this test?
• Under the exposure conditions in typical home heating systems – is there a clear problem with the continued use of copper?
• With increased use of biodiesel – is the copper concern greater?
Background: Copper Exposure Scenarios

- **One pipe system** with a copper feed line
  - All fuel is burned immediately after exposure
  - Winter: All fuel is exposed for a very short time.
  - Spring/Fall: Most of the fuel is exposed for a very short time; a small amount of fuel can remain in the fuel line for hours between burner firings.

- **Two pipe system** with a copper feed line
  - All fuel is exposed but not all is burned immediately
  - A portion of the fuel circulates back to the fuel tank
  - Impact of copper could be transferred to the bulk fuel in the tank.

- **Heat-only systems** (i.e., furnace only) with a copper feed line
  - A small amount of fuel remains in the line for the summer months

  Note – it is very common to collect fuel samples for testing from the pump bleeder valve at which point the fuel has been exposed, if a system has a copper feed line.
Measurements

• Oxidative Reserve (Rancimat) – EN15751 (per ASTM D396)
• Long Term Storage Stability – ASTM D4625
• Filterable Particulates – ASTM D6217
• Trace metals in fuel – ICP
Tube Test – Fuels Exposed in a Vertical Copper Tube

Test – 24 hr exposure at room temperature (at NORA lab)

<table>
<thead>
<tr>
<th>Fuel sample</th>
<th>Control (not exposed)</th>
<th>Exposed</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 2 oil</td>
<td>18.3</td>
<td>3.1</td>
</tr>
<tr>
<td>B20</td>
<td>8.2</td>
<td>1.0</td>
</tr>
<tr>
<td>B50</td>
<td>7.8</td>
<td>0.1</td>
</tr>
<tr>
<td>B100</td>
<td>6.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Oxidative Reserve (Rancimat) Testing [hr]
Tube Test – Fuels Exposed in a Vertical Copper Tube

Test – 24 hour exposure at room temperature (at REG lab)

<table>
<thead>
<tr>
<th>Test</th>
<th>Control</th>
<th>Exposed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidative Reserve (Rancimat)</td>
<td>7.6 hrs</td>
<td>0.2 hrs</td>
</tr>
<tr>
<td>Copper content [ppm]</td>
<td>&lt; LOQ</td>
<td>4.1</td>
</tr>
<tr>
<td>Zinc content [ppm]</td>
<td>&lt; LOQ</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Long Term Storage Test – 9 weeks

<table>
<thead>
<tr>
<th>Fuel (avg of 2 each)</th>
<th>Filterable Insolubles</th>
<th>Adherent Insolubles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
<td>Exposed</td>
</tr>
<tr>
<td>No. 2 oil</td>
<td>0.4</td>
<td>8.8</td>
</tr>
<tr>
<td>B20</td>
<td>0.25</td>
<td>5.8</td>
</tr>
</tbody>
</table>
Long Term Storage Test – No. 2 oil (B0)

No. 2 Oil at week 12

Effect of Copper Exposure on No. 2 Fuel Oil

Adherent Insolubles (mg/100 mL)

Filterable Insolubles (mg/100 mL)

- Filterable Insolubles
- Adherent Insolubles

Weeks

3  6  9  12
Two-pipe tank test – running for 2 months

Experimental set-up:
• Two pipe configuration with fuel tank
• 25’ of 3/8” copper tube for both supply and return
• Pump ran continuously
• ~75 gallons of No. 2 fuel
• Samples taken from the pump bleeder
Two-pipe tank test – tubes idle for 2 months

• After the 2-month pump run test, the fuel sat idle in the two lines for an additional 2 months to emulate summer shutdown
• After this period the fuel was removed from the lines for analysis

**Fuel test results:**
- Oxidative Reserve: 13.45 hrs
- TAN: 0.025 mg KOH/g
- Copper content: ~0.2 ppm
Conclusions

• If fuels are sampled from the pump bleeder, after exposure to copper fuel lines, the measured oxidative reserve may be influenced by the copper and may not represent the fuel in the tank.

• If fuel is exposed to fresh copper at a high surface to volume ratio, even for a relatively short time, very small amounts of dissolved copper can affect the measured oxidation stability value.
  • This occurs with fuel oil and biodiesel blends
  • Potential long term impacts for B20 were less than B0 in this study

• Under typical tank – fuel line conditions, the impact of copper exposure on the bulk of the fuel in the tank has not been found to be very significant