Understanding improvements to low temperature rheology of stiff binders modified with epoxidized plant derived oil materials through analytical chemistry

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• Asphalt is a co-product derived during the refining of crude petroleum.

• Commonly used base asphalt binders in the United States are produced as a co-product in Atmospheric Distillation Units (ADU).
Asphalt binders produced at refineries are becoming stiffer due to increase demand for lighter fraction products such as gasoline and jet fuel.
Introduction

- Great potential for epoxidized plant oil materials can improve the rheology of stiff binders.
  - Feasible economic alternatives to commonly produced base binders.
- Three stiff asphalt binders produced from:
  - Vacuum Distillation (VD) tower
  - Solvent Deasphalting (SDA)
  - Residuum Oil Super critical Extraction (ROSE).
- Recent work showed that epoxidized plant oil materials helped spread the continuous grade range while making the high grade lower and improving the low grade significantly.
- Further understanding through analytical chemistry.
Materials

• Three control binders:
  – **VD Tower Bottoms (C1)** from Ohio Refinery, Pen Grade 10-20.
  – **SDA Unit Bottoms (C4)** from Utah Refinery, Pen Grade 0-5.
  – **ROSE Unit Bottoms (C7)** from New Mexico Refinery, Pen 0.

• Used for modification:
  – **Epoxidized Benzyl Soyate (EBS)**
  – **Epoxidized Methyl Soyate (EMS)**
    • 8% to the VD tower bottoms (C2 and C3)
    • 12% to the SDA unit bottoms (C5 and C6)
    • 15% to the ROSE unit bottoms (C8 and C9)
<table>
<thead>
<tr>
<th>Group Code</th>
<th>Base Asphalt</th>
<th>Dosage/Material</th>
<th>Critical High Temperature (Unaged) (°C)</th>
<th>Critical High Temperature (RTFO) (°C)</th>
<th>Critical Low Temperature (PAV) (°C)</th>
<th>PG</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>VD</td>
<td>None</td>
<td>89</td>
<td>89.3</td>
<td>-11</td>
<td>88-10</td>
</tr>
<tr>
<td>C2</td>
<td>VD</td>
<td>8% EBS</td>
<td>70</td>
<td>70</td>
<td>-24</td>
<td>70-22</td>
</tr>
<tr>
<td>C3</td>
<td>VD</td>
<td>8% EMS</td>
<td>67.2</td>
<td>69.6</td>
<td>-23.7</td>
<td>64-22</td>
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<tr>
<td>C4</td>
<td>SDA</td>
<td>None</td>
<td>103.4</td>
<td>106.9</td>
<td>27.2</td>
<td>100+32</td>
</tr>
<tr>
<td>C5</td>
<td>SDA</td>
<td>12% EBS</td>
<td>71.8</td>
<td>77.6</td>
<td>-13.8</td>
<td>70-10</td>
</tr>
<tr>
<td>C6</td>
<td>SDA</td>
<td>12% EMS</td>
<td>68.9</td>
<td>76.4</td>
<td>-14.8</td>
<td>64-10</td>
</tr>
<tr>
<td>C7</td>
<td>ROSE</td>
<td>None</td>
<td>104.7</td>
<td>103.8</td>
<td>28.8</td>
<td>100+32</td>
</tr>
<tr>
<td>C8</td>
<td>ROSE</td>
<td>15% EBS</td>
<td>67.5</td>
<td>69.7</td>
<td>-18.6</td>
<td>64-16</td>
</tr>
<tr>
<td>C9</td>
<td>ROSE</td>
<td>15% EMS</td>
<td>58.6</td>
<td>62</td>
<td>-21.3</td>
<td>58-16</td>
</tr>
</tbody>
</table>
• Unaged and PAV aged binders
  — Settings used for testing:
    • resolution – 2cm\(^{-1}\),
    • sample scan time – 16 scans,
    • saved data from 4000 to 855 cm\(^{-1}\),
    • scanner – 5kHz,
    • aperture setting – 6mm,
    • laser wavelength – 15800.36, and
    • phase resolution – 32.
  — Specimen preparation described in more detail in paper.
FTIR-ATR Results

- The carbonyl index is defined as:

\[ I_{CO} = \frac{V_{CO}}{V_{r}} \times 100 \]

- Where, \( I_{CO} \): Carbonyl index (%), \( I_{SO} \): \( V_{CO} \): Carbonyl peak area, \( V_{r} \): Methyl + ethyl peak area.

- Area of the carbonyl peak was calculated between wavenumbers 1753 cm\(^{-1}\) and 1660 cm\(^{-1}\).

- Areas of the ethyl and methyl peak areas were calculated as the area under the FTIR spectrum between wavenumbers 1525 cm\(^{-1}\) and 1350 cm\(^{-1}\), as outlined in the French MLPC Method No. 69.

Rate of aging is lower for the VD bottoms modified with EMS and EBS than the control VD, where EBS has the lowest rate of aging.
Rate of aging is higher for the SDA control bottoms than the SDA groups modified with EMS and EBS, with EMS having the lowest rate of aging.
Rate of aging is similar between the control ROSE bottoms and ROSE bottoms modified with EBS and EMS. However, the control ROSE bottoms still has the lowest rate of aging, while EMS has the highest.
• Rates of oxidative aging seen by the modified VD binders with EBS and EBS are still much higher than the rate of oxidative aging seen for the SDA and ROSE modified binders with EBS and EMS.
• EBS and EMS are interacting with a chemical component/components in all three control binders, but are having a much greater influence in making the SDA and ROSE binders less susceptible to oxidative aging.
• To further investigate this, mass spectrometry utilizing ion mobility was done on the nine groups of binders.
Specimen preparation of unaged binders

- 50 mg asphalt binder transferred to a glass vial for accurate weighing.
- Toluene added to prepare stock samples that were 10.0 mg/mL in concentration.
- Aliquot of stock was diluted with toluene and methanol to form a sample that was 2 mg/mL in concentration in 90/10 (v/v) toluene/methanol.
ASAP IM-MS

• Test Parameters
  – Positive Ion ASAP
  – MS Spectra from m/z = 50 to 1200
  – Corona Pin Current = 20 μA
  – IMS Wave Velocity = 1200 m/sec
  – IMS Wave Height = 40 V
  – Cone Voltage = 40 V
  – Source = 120 °C
  – Desolvation Gas Flow = 400 L/hr
  – Cone Gas Flow = 75 L/hr

• ASAP Temperature Step Ramp = 50 to 650 °C

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to 1.0</td>
<td>50 °C</td>
</tr>
<tr>
<td>1.0 to 2.0</td>
<td>250 °C</td>
</tr>
<tr>
<td>2.0 to 3.0</td>
<td>350 °C</td>
</tr>
<tr>
<td>3.0 to 4.0</td>
<td>450 °C</td>
</tr>
<tr>
<td>4.0 to 5.0</td>
<td>550 °C</td>
</tr>
<tr>
<td>5.0 to 6.0</td>
<td>650 °C</td>
</tr>
</tbody>
</table>

• Probe inserted at 0.5 minutes
ASAP IM-MS Results

- 9 comparisons were made for the control and modified binders using the program HDMS Compare.
- Comparison is between two binders.
- Differences and similarities between the control binders themselves should be examined more thoroughly.
- For this probability heat maps were used in HDMS Compare.
ASAP IM-MS Results

- Majority of the differences occurred between mass spectrum locations m/z 200 and m/z 500 from 30 to 80 drift time bins when comparing C1 to C4, and C1 to C7.
Identification of similarities between C4 and C7 that show up as differences between C1 and C4, and C1 and C7.

Using HDMS Compare it was found that the area of interest in binders C4 and C7 is between drift time bins 30 and 60, and mass spectrum locations m/z 250 and m/z 400.

It is believed the EBS and EMS are more effective at improving the critical low temperature than reducing the critical high temperature for the SDA and ROSE unit binders because of these molecules.
Conclusions & Future Work

• There are molecules in the SDA and ROSE binders that is interacting with both EBS and EMS, and making them perform more aggressively.

• FTIR-ATR results show that the effect on oxidative aging is not the same between the three binders when modified with EBS and EMS, and that both materials either keep the same level of oxidative aging as the control or decrease the rate of oxidative aging in the SDA and ROSE binders.

• From ASAP IM-MS work and analysis the area of interest for future examination within the base binders, SDA and ROSE, is between m/z 250 and m/z 400.

• It is believed that the chemical components causing the EBS and EMS to perform more aggressively are within this range of the mass spectrum.
Questions?
Thank You!