Bitumen Blending, Oxidation, and Quality Requirements

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Latest Technological Advances in Bitumen Testing and Evaluation

• Bitumen sources and chemistry
• What is the risk in blending sources
• What is the risk in blending grades
• How can we control quality of blended bitumen
Production of Pen and Roofing Grades

Softer Grades - Pen 100-200

Harder Grades – Pen 10-20

Penetration at 25 C

Softening Point, C
http://www.eurobitume.eu/bitumen/production-process
The Three Main Processes of Bitumen Production

Distillation
The most common refining process is **straight reduction** from crude or a crude blend, using **atmospheric and vacuum distillation**. To remove the last traces of the lighter fractions and avoid heat transformation of the molecules. Vacuum distillation is for pressure reduction to lower boiling temperatures and unwanted thermal cracking of the molecules can be avoided.

Solvent de-asphalting
Specific solvents can also be used to **separate the lubricant and bitumen components** of crude, without damaging their chemical structure. Along with finely controlled variations in the vacuum distillation process, these processes permit the production of bitumens with varying levels of penetration.

Oxidation
Bitumen can be further processed by blowing air through it at elevated temperatures (280°C on average) to alter its physical properties for commercial applications. Oxidised bitumen covers two distinct types depending on the degree of oxidation: **air rectified and oxidised**. Varying the length of the oxidation or air blowing process varies the extent of the reaction and produces distinctive end products. Oxidised bitumen is used in roofing applications, while air rectified bitumen is used in paving applications and some roofing applications.
Pitch- Cracking of Petroleum Fractions

- Bitumen is sometimes confused with petroleum pitch which is also derived from crude oil.
- Pitch is the residue from the extreme heat treatment or “cracking” of petroleum fractions.
- The properties and chemical composition are quite different from those of bitumen.
- Pitch blending could be high risk for bitumen quality.
The Blending of Bitumen Products

The final bitumen product can be produced to technical specification either:

1. Directly in the refining process or by blending bitumens with different physical properties.
2. Blending of higher and lower viscosity residues in the required proportions.
3. The blending may take place at the refinery, at terminals or at a third party facility.

Finished products can be easily transported and distributed for use.
Asphalt Molecular Structure
A Delicate Balance of Chemistry
Asphalt Molecular Structure Hypothesis

- **SOL**
- **SOL-GEL**
- **GEL**

**INCREASING ASPHALTENES**

**ASPHALTENES**

**RESINS**

**SATURATES**

**HIGH POLARITY**

**LOW POLARITY**

**PEPTIZATION**
Risks to Quality

- **Blending from different sources** could be a problem. Not all chemistries are similar.
- **Oxidation changes chemistry**, molecular weight, and could upset balance of bitumen.
- **De-asphalted bitumen** is not really a paving grade material.
- **It is very hard to tell when Pitch** is used in bitumen production.
- **Soft bitumen-Vacuum Tower Bottoms (VBTs)** are abundant.
Examples of VTB based feed stock in the GCC region

<table>
<thead>
<tr>
<th>Property</th>
<th>Source 1</th>
<th>Source 2</th>
<th>Source 3</th>
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</thead>
<tbody>
<tr>
<td>Pen at 25 C, dmm</td>
<td>119</td>
<td>169</td>
<td>60</td>
</tr>
<tr>
<td>R&amp;B Softening Pt, °C</td>
<td>43</td>
<td>34</td>
<td>51</td>
</tr>
<tr>
<td>Ductility, cm</td>
<td>84</td>
<td>&gt;125</td>
<td>&gt;125</td>
</tr>
<tr>
<td>Flash point, C</td>
<td>321</td>
<td>328</td>
<td>346</td>
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<tr>
<td>R. Vis at 135C</td>
<td>212</td>
<td>100</td>
<td>388</td>
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</tbody>
</table>
Fig. 4. Diagrammatic sketch of particles in asphalt types: (a) sol asphaltenes; (b) sol-gel asphaltenes; (c) gel asphaltenes.
Bitumen Compatibility

- Highly related to production
- Best is straight run
- All blending steps impose risks
- Within a refinery is the least risk
- Too hard + too soft is the highest risk

Source: Shell Handbook
Viscosity Blending Chart

- Blend A - Hard
- Blend C - Soft
- Log Viscosity versus % blend
Development a simple blend chart

\[ y = 0.0133x + 3.2197 \]

\[ R^2 = 0.9931 \]
Example for Blending of PG Binders with different Grades

$$G^* \sin d$$

Limiting Temperature, $C$

Hard Bitumen

RAP PG (xx-04)

Fresh Bitumen

$S(6), m(60)$

PG (xx-28)

(% Fresh Bitumen) 100 %

24 $C$
Checking Quality of Blends - Spot Test

A spot of bitumen is placed on a filter paper and several drops of a special solvent are washed over the sample. After a short time the solvent is seen to form a brown ring around the bitumen drop. If a black ring develops within the brown ring the test is deemed to be positive, otherwise it is negative.

This test was developed to detect cracked petroleum residues in bitumen formed during excessive heating of the bitumen. However, it is now known that some crudes produce bitumens which give positive results in this test.
Hot Storage Test- Poor blends will Separate
Rheology can be used to detect problems and establish consistency.

![Graph showing rheological properties of materials under different conditions.](image_url)
New / advanced testing proposed for modified bitumens

1. Viscosity at variable shear rate
2. Binder repeated creep
3. Binder fatigue
4. Fracture glass transition
5. Cohesion

Pavement Temperature, C

PAV
RTFO
Bitumen Grading System - PG

1. Climate
2. Traffic conditions - Trucks
3. Reliability, and
4. Cost/Modification

Traffic
Volume & Speed

PG 76 (X) - 10

Performance Grade

Summer
Average 7-day max pavement design temp

Winter
Min pavement design temp

 PG 76 (X) - 10

Performance Grade

1. Climate
2. Traffic conditions - Trucks
3. Reliability, and
4. Cost/Modification

Traffic
Volume & Speed
Measuring Molecular Structure – Chromatography (GPC)

Amoco 309 GPC Analysis

<table>
<thead>
<tr>
<th></th>
<th>Soft</th>
<th>Very Hard</th>
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<tbody>
<tr>
<td>Molecular Weight Averages</td>
<td></td>
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</tr>
<tr>
<td>Mp</td>
<td>1058</td>
<td>862</td>
</tr>
<tr>
<td>Mn</td>
<td>640</td>
<td>1049</td>
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<tr>
<td>Mw</td>
<td>1868</td>
<td>6891</td>
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<tr>
<td>Mz</td>
<td>4910</td>
<td>29239</td>
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<tr>
<td>Mz+1</td>
<td>9783</td>
<td>52106</td>
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<tr>
<td>Mv</td>
<td>1609</td>
<td>5114</td>
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<tr>
<td>Polydispersity</td>
<td>2.919</td>
<td>6.567</td>
</tr>
<tr>
<td>(Mw/Mn)</td>
<td></td>
<td></td>
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<tr>
<td>Area (Response Minutes):</td>
<td>1.29E+06</td>
<td>1.29E+06</td>
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</tbody>
</table>

- Fresh Soft Bitumen
- Air rectified
- Oxidized
- Pitch / PPB

Molecular Size Indicator

Relative Amount

Molecular Weight Averages

Molecular Weight

Coating

Aged Panel Rep

1

Aged Panel Rep

2

Mp   1058  862  939  1005
Mn   640  1049 1133 1360
Mw   1868 6891 7966 11867
Mz   4910 29239 30078 51421
Mz+1 9783 52106 57967 104629
Mv   1609 5114 6102 8810
Polydispersity (Mw/Mn) 2.919 6.567 7.028 8.726
Area (Response Minutes): 1.29E+06 1.29E+06 1.48E+06 1.56E+06
Concluding Remarks - Bitumen Blending

- **Straight-run bitumen** is simplest and most consistent
- Oxidation, rectification, de-asphalting and cracking are common refinery practices that present risk to quality
- **Blending will continue** to be used to provide bitumen, **Mixing of sources** is very risky
- Measures to check quality and prevent poor quality need to be practiced
- Chemical, **rheology and GPC** are potential quality control tools
- **Performance grading (PG)** is one of the good tools
Thank You

- Organizers of the conference
- Sponsors /partners of MARC

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