Parviz Rahimi

National Centre for Upgrading Technology (NCUT)

Parviz Rahimi obtained his PhD in Chemistry from the University of Alberta in 1980 and joined Natural Resources Canada in 1981. Currently he is working as senior research scientist in the primary upgrading division of the National Centre for Upgrading Technology (NCUT) in Alberta, Canada.

His expertise in bitumen chemistry extends beyond molecular characterization into upgrading processes including field upgrading. He has extensive knowledge of partial upgrading either using thermal conversion such as visbreaking or partial deasphalting for the purpose of reducing the required diluent for pipeline transportation. He has established an expert team to address the stability and compatibility issues related to partially upgraded bitumen and heavy oils as well as during production and upgrading. His recently research activities include fouling and corrosion related to bitumen processing. He has established networking research into understanding bitumen/heavy oil processing with Universities, Government departments and private research organizations as well as major oil companies.

National Centre for Upgrading Technology (NCUT)
1 Oil Patch Drive
Devon, Alberta T9G1A8 Canada
Phone: 1 780 987 8708
Fax: 1 780 987 5349
Email: Parviz.Rahimi@nrcan.gc.ca
Website: www.canmetenergy.nrcan.gc.ca
Diluent Evaluation for Bitumen Pipelining

Parviz Rahimi, Simon Cooper, Telemariam Alem
National Centre for Upgrading Technology (NCUT)

Oil sands crudes are expected to represent more than 75% of the crude produced in Western Canada. The bitumen are too viscous and must be diluted with a lighter hydrocarbon stream to meet the specifications required for shipping in pipelines, i.e., viscosity 350cSt (11°C) and gravity 19 °API, etc. Thermal processing could reduce the viscosity of the bitumen crudes and thus require less diluent but produces less stable fuels. It is expected that there will be a shortage of local diluent for pipeline transportation of bitumen which leads to demand for imported and recycled diluents. Compatibility and stability characteristics when blending diluents and crudes are important issues in the pipeline transportation.

The objectives of this work are:

- Investigation of the compatibility and stability of virgin and cracked bitumen in natural diluents and synthetic diluents
- Diluents ranking for asphaltenes stability in virgin bitumen, cracked bitumen

Four heavy oils and bitumens where used in this study – Athabasca bitumen (AB), cracked Athabasca bitumen, heavy oil B, and a light crude C were chosen to investigate their compatibility and stability characteristics with two different diluents, i.e. natural gas condensate (NGC), oil sands derived liquid (Synthetic).

Following oil compatibility model developed by Irwin Wiehe, the insolubility number and solubility blending number of different crudes, diluents and their blends were investigated. Using an optical method it was shown that the stability of different heavy oils can be accurately determined and ranked by observing flocculation of asphaltenes. Similarly the strength of different diluents including natural gas condensates and synthetic diluents for keeping asphaltenes soluble in the oil matrix were evaluated and ranked. It was shown while synthetic diluents are better solvents than NGC for bitumen, when bitumen is processed the order of the solvent strength is reversed. The reason for this behavior will be discussed.
Diluent Evaluation for Pipelining

Parviz Rahimi, Zhiming Fan, Simon Cooper, Teclemariam Alem, National Centre for Upgrading Technology (NCUT) and
Irwin Wiehe
Soluble Solutions

For presentation at
5th NCUT Upgrading and Refining Conference 2009

Edmonton, Alberta
September 14-16, 2009
Outline

- Background
- Objectives
- Bitumen – solvent Compatibility
- Asphaltenes stability in different solvent
- Conclusions
Background

- Bitumen production is increasing:
  - Current: 1.5 MMBD
  - 2015: 3.0 MMBD
  - 2030: 5.0 MMBD
Heavy oils in western Canada are characterized by:

- High viscosity \( >100,000 \text{ cP} \)
- High gravity 7-15 °API
- High asphaltenes 17 wt% (C\(_5\))
- High aromaticity 0.33

**Pipeline Specifications**

- Viscosity 350 cSt @ 11°C
- Gravity 19 °API
Pipeline Transportation - Issues

• Heavy oils/bitumens are too viscous and require diluent for pipeline transportation

• Thermal processing will reduce viscosity (less diluent required) but produces less stable fuel

• Shortage of local diluent for pipeline transportation of bitumen leads to demand for imported and recycled diluent

• Compatibility between diluents and bitumens/heavy oils is an important issue that should be addressed
Objectives

- Investigate the compatibility and stability of virgin and cracked bitumen in:
  - Natural diluents
  - Synthetic diluents

- Diluents ranking for asphaltenes stability in virgin bitumen, cracked bitumen
Feedstocks

- **Oils:**
  - Athabasca Bitumen (AB)
  - Cracked AB (bottoms)
  - Bitumen B
  - Light crude (C)

- **Diluents:**
  - Natural Gas Condensate (NGC) - Dilbit
  - Oil Sands-derived liquid - Synbit
  - N-alkanes
Properties of Diluents

- Natural Gas Condensate (NGC) - Dilbit
- Oil sand-derived liquid - Synbit

<table>
<thead>
<tr>
<th></th>
<th>Naphthenes (wt%)</th>
<th>Paraffins (wt%)</th>
<th>Aromatics (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(wt%)</td>
<td>Iso</td>
<td>Norm</td>
</tr>
<tr>
<td>NGC</td>
<td>19.0</td>
<td>40.0</td>
<td>35.0</td>
</tr>
<tr>
<td>Synthetic</td>
<td>28.6</td>
<td>29.1</td>
<td>33.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbon #</th>
<th>NGC</th>
<th>Syn</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.10</td>
<td>3.67</td>
</tr>
<tr>
<td>5</td>
<td>38.9</td>
<td>11.1</td>
</tr>
<tr>
<td>6</td>
<td>30.6</td>
<td>15.1</td>
</tr>
<tr>
<td>7</td>
<td>16.9</td>
<td>17.3</td>
</tr>
<tr>
<td>8</td>
<td>7.28</td>
<td>18.1</td>
</tr>
<tr>
<td>9</td>
<td>3.15</td>
<td>17.4</td>
</tr>
<tr>
<td>10</td>
<td>1.19</td>
<td>11.6</td>
</tr>
<tr>
<td>11</td>
<td>0.90</td>
<td>5.72</td>
</tr>
</tbody>
</table>
# Properties of the Oils

- Athabasca Bitumen (AB)
- Cracked AB (bottoms)
- Bitumen B
- Light crude (C)

<table>
<thead>
<tr>
<th></th>
<th>AB</th>
<th>Cracked AB</th>
<th>Bitumen B</th>
<th>Light Crude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturates</td>
<td>20.5</td>
<td>23.6</td>
<td>n/a</td>
<td>61.8</td>
</tr>
<tr>
<td>Aromatics</td>
<td>48.5</td>
<td>53.2</td>
<td>n/a</td>
<td>29.6</td>
</tr>
<tr>
<td>Polars</td>
<td>12.9</td>
<td>12.7</td>
<td>n/a</td>
<td>7.5</td>
</tr>
<tr>
<td>C₅ insoluble</td>
<td>18.1</td>
<td>10.5</td>
<td>17.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>17.4</td>
<td>100</td>
</tr>
</tbody>
</table>
Bitumen – Diluent Compatibility
Asphaltenes Stability – Optical Method

- ASTM D- 7157
- ASTM D- 6703
- ASTM D- 7060
- ASTM D- 7061
Compatibility Model

Developed by Irwin Wiehe to determine crude incompatibility that causes fouling and coking

\[ I_N = \frac{TE}{1 - \frac{V_H}{25d}} \]
\[ S_{BN} = I_N \left( 1 + \frac{V_H}{5} \right) \]

- \( S_{BN} \) – Solubility Blending Number – a measure of the oil solvency for asphaltenes
- \( I_N \) – Insolubility Number – a measure of asphaltene solubility
- \( d \) - Density

For compatible blends: \( S_{BN} > I_N \)
Laboratory Test Based on Toluene – Heptane Scale

- **TE** – minimum vol% of toluene in test liquid (toluene/n-heptane mixture) to keep asphaltenes in solution at a concentration of two grams of oil and 10mL of test liquid.

- **$V_H$** – the maximum volume of heptane that can be blended with 5mL of oil without precipitating asphaltenes.
Solubility Parameters

\[
I_N = \frac{TE}{1 - \frac{V_H}{25d}}
\]

\[
S_{BN} = I_N \left(1 + \frac{V_H}{5}\right)
\]

For compatible blends: \( S_{BN} > I_N \)
Compatibility Model

Predicted solubility numbers for blends

\[ S_{BN_{blend}} = \frac{V_A S_{BN(A)} + V_B S_{BN(B)}}{V_A + V_B} \]
## Compatibility of Synthetic Diluent with Athabasca Feed

<table>
<thead>
<tr>
<th>Volume of Synthetic</th>
<th>Volume AB Feed</th>
<th>$S_{BN_{mix}}$</th>
<th>P-Value ($S_{BN}/I_N$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>85.5</td>
<td>3.02</td>
</tr>
<tr>
<td>5</td>
<td>95</td>
<td>82.2</td>
<td>2.90</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>72.2</td>
<td>2.55</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>65.5</td>
<td>2.31</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>58.8</td>
<td>2.08</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>52.2</td>
<td>1.84</td>
</tr>
<tr>
<td>65</td>
<td>35</td>
<td>42.2</td>
<td>1.49</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>38.8</td>
<td>1.37</td>
</tr>
<tr>
<td>85</td>
<td>15</td>
<td>28.14</td>
<td>1.02</td>
</tr>
</tbody>
</table>

- **Solubility ($S_{BN}$):** 18.8
- **Insolubility ($I_N$):** 0
- **Non-solvent oil**
Compatibility of NGC with Athabasca Feed

<table>
<thead>
<tr>
<th>Volume NGC</th>
<th>Volume AB Feed</th>
<th>$S_{BN}^{\text{mix}}$</th>
<th>P-Value ($S_{BN}/I_N$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>85.5</td>
<td>3.02</td>
</tr>
<tr>
<td>5</td>
<td>95</td>
<td>81.5</td>
<td>2.88</td>
</tr>
<tr>
<td>15</td>
<td>85</td>
<td>73.5</td>
<td>2.60</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>65.4</td>
<td>2.31</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>59.5</td>
<td>2.17</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>53.4</td>
<td>1.89</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>45.3</td>
<td>1.60</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>37.3</td>
<td>1.32</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>29.3</td>
<td>1.03</td>
</tr>
</tbody>
</table>

NGC

Solubility ($S_{BN}$) = 5.2
Insolubility ($I_N$) = 0

AB Feed

Solubility ($S_{BN}$) = 85.5
Insolubility ($I_N$) = 28.3

Non-solvent oil
# Compatibility of Synthetic Diluent with Cracked AB Feed

<table>
<thead>
<tr>
<th>Synthetic</th>
<th>Volume of Synthetic</th>
<th>Volume C-Feed</th>
<th>SBN\textsubscript{mix}</th>
<th>P-Value (S\textsubscript{BN}/I\textsubscript{N})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cracked Feed</td>
<td>0</td>
<td>100</td>
<td>101.1</td>
<td>1.22</td>
</tr>
<tr>
<td>5</td>
<td>95</td>
<td>97.0</td>
<td>1.17</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>92.9</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>85</td>
<td>88.8</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>84.7</td>
<td>1.02</td>
<td></td>
</tr>
</tbody>
</table>
### Compatibility of NGC with Cracked AB Feed

<table>
<thead>
<tr>
<th>Volume NGC</th>
<th>Volume C-Feed</th>
<th>( S_{BN}^{\text{mix}} )</th>
<th>( S_{BN}/I_N )</th>
<th>P-Value (( S_{BN}/I_N ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>101.1</td>
<td></td>
<td>1.22</td>
</tr>
<tr>
<td>5</td>
<td>95</td>
<td>96.0</td>
<td></td>
<td>1.16</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>91.0</td>
<td></td>
<td>1.10</td>
</tr>
<tr>
<td>15</td>
<td>85</td>
<td>86.7</td>
<td></td>
<td>1.05</td>
</tr>
<tr>
<td>NGC</td>
<td>5.2</td>
<td>0</td>
<td>Non-solvent oil</td>
<td></td>
</tr>
<tr>
<td>Cracked Feed</td>
<td>101.12</td>
<td>82.88</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Condensate Requirement

![Graph showing the relationship between Vol% condensate and Solubility numbers for Visbroken and Bitumen samples. The graph illustrates a linear decrease in solubility numbers as the Vol% condensate increases.]
Asphaltenes Stability in Different Solvents
Equipment - Turbiscan AGS

- The Turbiscan AGS is a fully automated near-infra red (880nm) optical scanner
- Capable of fully scanning a sample once a minute with scans at 40µm intervals
- Temperature Control
Turbiscan AGS

Simultaneous Transmission (T%) and Backscatter (BS%) Profile
Sample Preparation

- **Basic sample preparation modified from ASTM D7061**
  - 10g Oil + 90g Toluene (1:9)
  - magnetic stir 1-3hr
  - 4mL Oil/Toluene + 46mL precipitant
  - shake for 6s and immediately add 20mL of solution to vial
  - Insert vial for immediate scanning
Turbiscan Data Output

Cracked Bitumen / Heptane

heptane & ahs (25C-8m1d)_1 - [File created by Turbisoft-AGS Version 1.1 English]  (01/08/07 16:50:30)

Transmission - No zoom

Backscattering - No zoom

Temperature - No zoom

Control point

Set point
**Interpretation of Data**

- Profile changes are due to changes in the localized concentration of particles and changes in the average particle size.

- Separability number (Eqn. 1) (ASTM D7061) can be calculated from data as a measure of stability.

\[
\text{Separability number} = \sqrt{\frac{\sum_{i=1}^{n} (X_i - X_T)^2}{n - 1}}
\]

where:
- \(X_i\) = average transmittance for each 60 s,
- \(X_T\) = average of \(X_i\) \((X_T = X_1 + X_2 \ldots + X_{16}/16.\) and
- \(n\) = the set of replicate measurements (16 in the method).
Output Data Manipulation with Turbisoft

- Average percent Transmission values for each scan can be obtained and plotted versus time
N-alkanes with Cracked AB (1:9)
Comparison of oil stability ($n$-$C_7$)
Stabilization of Cracked AB by Maltenes

- M/C = 0/1, SN = 11.3
- M/C = 0.5/1, SN = 9.2
- M/C = 1/1, SN = 6.8
Separability vs Asphaltene Content

- Virgin Oils with higher amounts of asphaltenes are more stable than processed oils
- Light oils with low asphaltenes are unstable

<table>
<thead>
<tr>
<th>Oil</th>
<th>C₅ Insoluble (wt. %)</th>
<th>Separability Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>18.1</td>
<td>5.4</td>
</tr>
<tr>
<td>Bitumen B</td>
<td>17.3</td>
<td>5.5</td>
</tr>
<tr>
<td>Cracked AB</td>
<td>10.5</td>
<td>11.4</td>
</tr>
<tr>
<td>Crude A</td>
<td>1.2</td>
<td>8.2*</td>
</tr>
</tbody>
</table>

* Light oil - oil/toluene=1:1
Stability Effects of Diluents

AB + Diluents

Cracked + Diluents

Crude A + Diluents

Transmission %

Time, t, min

NGC

Synthetic

C_7

Transmission %

Time, t, min

NGC

Synthetic

C_7

Transmission %

Time, t, min

NGC

Synthetic
Conclusions

Compatibility data:
• Oil sands-derived liquids are better solvent for bitumen than NGC
• With cracked feed lower volume of both Synthetic solvent and NGC result in incompatibility

Stability data:
• Using an automated Turbiscan it is possible to compare and rank stability of oils and diluents
• Asphaltenes stability studies showed:
  – For cracked feed NGC is a better solvent than oil sands-derived solvent
  – For Athabasca bitumen oil sands-derived solvent is better than NGC
Acknowledgements

This work was supported by:

NCUT: PERD and AERI