BIOGRAPHY

Thomas W. McCracken

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EDUCATION:

M.A.Sc. (Chemical Engineering), University of Toronto, Canada
B.A.Sc (Chemical Engineering), University of Toronto, Canada

EXPERIENCE:

Extensive experience in oil sands processing application including development of feed injection systems for coker reactors and development of novel bitumen extraction and upgrading processes. Has published more than 65 scientific articles, written 35 reports and presented the results of his work at over 50 scientific meetings. Also is inventor as co-author of 10 process and equipment patents. Now leading and coordinating oilsands R&D research for significant projects at NRC in collaboration with other government departments, academia and industry partners.

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AN INVESTIGATION OF PROBLEMATIC SOLIDS IN OIL SANDS PROCESSING - SEPARATION AND CHARACTERIZATION OF ORGANIC MATTER STRONGLY BOUND TO OIL SANDS SOLIDS

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¹V. Bede Technical Associates

In Athabasca oilsands certain solids fractions are associated with strongly bound organic matter insoluble in common organic solvents for bitumen such as toluene. This material is known as toluene insoluble organic matter or TIOM. Presence of TIOM increases oil wettability of solids and this may adversely affect the release of bitumen from the oilsands. The finest oil-wettable particles remain with the oil phase after bitumen separation. Some of this solid material is therefore carried over from the coking operation to downstream operations where it can be involved in fouling of those process units.

In this work, supercritical fluid extraction with methanol was used to remove TIOM from oilsands after extraction of bitumen by toluene. After removal from the solids the methanol extract (ME) is soluble in toluene. This allows for a detailed analysis of the ME by several advanced and complementary analytical techniques. The results are compared to similar data for the corresponding parent bitumen fractions prepared using a modified HPLC SARA separation technique.

Number average molecular weights for the ME are close to those for resins separated from bitumen. The number of alkyl substituents on aromatic ring systems and the lengths of paraffinic straight chains for resins and ME samples were found to be similar. Only minor differences exist between ME and the resins in terms of H/C atomic ratios and aromaticities. As indicated by the higher hetero atom contribution, the methanol extracts are more polar than the resin and asphaltene fractions. This may explain the apparent selective adsorption of this fraction, particularly through the predominant pyrrole and pyridine species.
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Background

• In Athabasca oil sands, certain solids fractions are associated with strongly bound organic matter insoluble in common organic solvents for bitumen such as toluene (resulting in toluene insoluble material or TIOM).

• Presence of TIOM increases oil wettability of solids and affects the release of bitumen from the oilsands.

• The finest oil wettable particles remain with the oil phase after bitumen separation -- Some of this solid material is carried over from the coking operation to downstream operations where it may contribute to fouling of process units.
Research Objectives

*To gain insight into chemical composition of TIOM:*

- Use of supercritical fluid extraction with methanol to separate TIOM from bitumen free oil sands solids.
- Fractionation of bitumen from corresponding oil sands using high performance liquid chromatography (HPLC).
- Use of complimentary advanced analytical techniques for comparative analysis of TIOM and bitumen fractions.
**Fractionation Methods**

**Supercritical fluid extraction (SCFE) of Solids**
- After removal from the solids the methanol extract was soluble in toluene
- This facilitated characterization and allowed direct comparison with fractions from the corresponding parent bitumen.

**High performance liquid chromatography (HPLC) of Bitumen**
After asphaltenes removal, fractionated bitumen into:
- Saturates
- Aromatics
- Three resin fractions (R1; R2; R3)
• After bitumen had been exhaustively extracted with toluene, oilsand solids were subjected to SFE with methanol.
• Extracted bitumen was separated into asphaltenes (asp) and maltenes.
• Application of HPLC to maltenes yields saturates (sat) aromatics (ar) and resins fractions.
• The resin component is divided into three fractions (R1, R2 and R3) based on increasing polarity (Fuel 2004, 83, 1907-1914).
• Supercritical methanol was delivered at a flowrate of 5 mL/min to a 50 mL extraction cell containing 50 grams of dried soxhlet extracted oilsand. The solvent was preheated to 250°C.

• The extraction cell temperature was also set at 250°C and system pressure was controlled to a constant 2000 psi by manually closing and opening a heated restrictor valve. The extract was collected into a 1 litre conical flask set in an ice bath for a total of 100 minutes.
Characterization Methods

**Molecular weights:**
GPC

**Elemental analysis:**
C,H,N,S with LECO analyzer

**Nitrogen and sulfur types:**
X-ray photo electron spectroscopy

**Carbon and proton types:**
$^{13}$C NMR, $^1$H NMR

**Average structural parameters:**
Calculated based on elemental analysis, MW and NMR results.
Parameters indicated similarities between the methanol extract and resins included:

- Cn ar (number of aromatic carbon atoms in molecule)
- Cn alfa (number of alkyl substituents on aromatic ring system)
- L (length of paraffinic straight chains)

Compared to resins, methanol extracts exhibited a lower degree of aromatic ring condensation (K).
Calculations based on molecular weights, elemental analysis, $^{13}$C NMR and $^1$H NMR.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cn ar</td>
<td>Number of aromatic carbon atoms in average single molecule</td>
</tr>
<tr>
<td>Cn alfa</td>
<td>Number of alkyl substituents on aromatic ring system in an average single molecule</td>
</tr>
<tr>
<td>K</td>
<td>Degree of condensation of aromatic ring system</td>
</tr>
<tr>
<td>L</td>
<td>Average paraffinic straight chains. Estimated from the ratios of the $^{13}$C NMR resonances at 29.7ppm and 14.2ppm.</td>
</tr>
</tbody>
</table>
Results

- Molecular weight of methanol extract (ME) and bitumen fractions
Results

- *Nitrogen in methanol extract (ME) and bitumen fractions*
Results

- **Sulfur in methanol extract (ME) and bitumen fractions**

![Bar chart showing sulfur content in different fractions.](chart.png)
• *Nitrogen and sulfur types in bitumen fractions and methanol extracts*

<table>
<thead>
<tr>
<th>Species</th>
<th>Species distribution in sample (% of total)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Resin (R3)</td>
</tr>
<tr>
<td>N Pyrrole</td>
<td>81.0</td>
</tr>
<tr>
<td>N Pyridine</td>
<td>19.0</td>
</tr>
<tr>
<td>S Thiophenic</td>
<td>74.0</td>
</tr>
<tr>
<td>S Sulphide</td>
<td>26.0</td>
</tr>
<tr>
<td>S Sulphoxide</td>
<td>bdl</td>
</tr>
<tr>
<td>S Sulphone</td>
<td>bdl</td>
</tr>
</tbody>
</table>

*bdl = below detection limit*
While pyrrole was always the primary nitrogen species, pyridine groups were also present in each case; the greatest contributions from pyridine species occurred in the ME samples.

In every case the sulphur species were predominantly thiophenic with some contribution from sulphides.

The sulphoxide and sulphone species occurred in only some of the asphaltene fractions from the parent bitumens; the highest concentrations of this species were found in the ME samples.

Concurrently with this observation the thiophenic sulfur contents in the methanol extracts are lower than those for the corresponding fractions from bitumen.
Results

- **Atomic H/C ratios for methanol extract (ME) and bitumen fractions**

<table>
<thead>
<tr>
<th>Sample</th>
<th>H/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>sat</td>
<td>1.8</td>
</tr>
<tr>
<td>ar</td>
<td>1.6</td>
</tr>
<tr>
<td>R1</td>
<td>1.4</td>
</tr>
<tr>
<td>R2</td>
<td>1.4</td>
</tr>
<tr>
<td>R3</td>
<td>1.2</td>
</tr>
<tr>
<td>Asp</td>
<td>1.2</td>
</tr>
<tr>
<td>ME</td>
<td>1.2</td>
</tr>
</tbody>
</table>


• $^{13}$C NMR aromaticity of methanol extract (ME) and bitumen fractions
Results

- *Number of aromatic carbon atoms in molecule (Cn ar)*
• **Degree of condensation of aromatic ring system (K)**
• *Number of alkyl substituents on aromatic ring system (Cn alfa)*
• **Length of paraffinic straight chain substituents (L)**
• *Fraction of carbon associated with oxygen* (fo)

fo estimated from the integration of the following $^{13}$C NMR regions (ppm)

<table>
<thead>
<tr>
<th>Region</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>50-70</td>
<td>Aliphatic C-OH, C-OR</td>
</tr>
<tr>
<td>145-160</td>
<td>Aromatic C-OH, C-OR</td>
</tr>
<tr>
<td>160-190</td>
<td>COOH, COOR, acid, ester</td>
</tr>
</tbody>
</table>

Conclusions

- Contributions of elemental nitrogen and carbon associated with oxygen for the methanol extract are higher than those measured for the resin and especially the asphaltene fractions from bitumen.
- In all cases, nitrogen species were predominantly pyrrolic. Pyrolle rich organic matter is known to undergo oxidative polymerisation to form the adhesive material with high propensity to fouling.
- Owing to its polar nature, TIOM may be responsible for increased interaction with bulk bitumen leading to associated difficulties with oil release and/or fouling during conventional water-based separation processes.
- Both elemental sulfur content and the contribution of thiophenic sulfur in the methanol extract samples is lower than those in the bitumen components.
Conclusions

• Molecular weights for methanol extracts from bitumen free oilsands solids are close to those for resin fractions, and much lower than those for asphaltenes.
• Only minor differences exist between methanol extract and the resins in terms of H/C atomic ratios and aromaticities.
• Number of aromatic carbon atoms in molecule, number and chain lengths of alkyl substituents on aromatic rings were among parameters pointing to similarities between the methanol extract and resins.
• Degree of condensation of aromatic ring systems for the ME samples are much lower than the values for the corresponding resin fraction.
• Both elemental sulfur content and the contribution of thiophenic sulfur in the methanol extract samples is lower than those in the bitumen components.
Acknowledgements

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Thank-you...