Recovery of Liquid Hydrocarbons from Oil Shale Using Supercritical CO$_2$

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Background

McGrady Group @ UNB

Hydrogen Storage

LiAlH$_4$ – US DOE ‘near-term material’

Oil Sands Processing

Supercritical fluid hydroprocessing of bitumen

Catalysis

Mn catalyst for hydrosilation

Smart Materials

Coloured conductive paper

Energy Efficiency and Renewable Energy
### SCF Hydroprocessing of Bitumen using Hexane or Pentane:

**Brough, Riley, McGrady et al. Chemical Communications (2010)**

**Sample** | **API Gravity (°)** | **H/C Ratio** | **Sulfur %** | **Viscosity (cP)** | **Asphaltenes %**
---|---|---|---|---|---
BITUMEN | 7.8 | 1.52 | 4.77 | 940,000 | 34.2
UPGRADED IN SC-HEXANE | 22.2 | 1.85 | 0.48 | 88 | 0.1
UPGRADED IN SC-PENTANE | 21.1 | 1.75 | 0.54 | 79 | 0.2

#### Background

**McGrady Group @ UNB**

**Asphaltenes**
- **36 %**

**Resins**
- **11 %**

**Saturates**
- **19 %**

**Aromatics**
- **34 %**

**Resins**
- **1 %**

**Saturates**
- **40 %**

**Aromatics**
- **59 %**

**BEFORE**

**AFTER**
Background

Oil sands/bitumen versus Oil shale/kerogen

- Petroleum has migrated from source-rock kerogen
- Bitumen ceased flowing in (fine-grained) sandstone
- Petroleum still retained in source-rock kerogen
- Kerogen interlaminated with (very-) fine grained siltstone

Some previous work by Kessavan et al. (1988) Stuart oil shale & others (2011) on Jordanian oil shale

From: Bianco et al. SEG Heavy Oil

UNB 15.0kV 15.1mm x1.00k SE(M)
Background

Keighley et al. @ UNB

- Albert Formation (New Brunswick) oil shale & tight-gas reservoirs (correlation & seq. strat.)
- Green River Formation shale, oil shale & sandstone (correlation & seq. strat.)
- CO₂ sequestration as a SCF in New Brunswick’s subsurface repositories (feasibility reports)
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1. Introduction to supercritical CO$_2$
2. Experimental set-up
3. Sample material
4. Early results
5. Summary
1. Introduction to supercritical CO₂

Total miscibility with permanent gases → Remarkable reactivity

Excellent thermal/mass transfer → Enhanced reaction rates

Low surface tension → High penetration of porous materials (supported catalysts)

Gas/Liquid Phases

Subcritical Phase

Supercritical Fluid (SCF)
2. Experimental set-up

Reaction Station for Supercritical Fluids

Roto-Evap

CHNS-932 Analyses

TGA (Thermal Gravimetric Analysis)

Remove solvents (& any produced light oils - yet to be measured)

IR detectors (@1050°C) for S content & H/C ratio

Gradual heating in N₂ for wt% & vacuum residue

10g rubbed sample & CO₂ for 16hrs

± solvent: THF, Toluene, Hexane, or (Sc) Pentane

2000psi @ 60°C or higher
3. Sample material

Albert Formation, New Brunswick

Previous retorting work @ Albert Mines (Altius-held lease)

Current sampling near Norton

clays (illite, smectite, kaolinite & chlorite), carbonate (dolomite, calcite & siderite), feldspar (albite & K-feldspar) quartz, analcime, pyrite
## 4. Early results

ScCO$_2$ extraction of oil from Albert oil shale

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Weight % of Shale</th>
<th>% Oil</th>
<th>H/C Oil</th>
<th>% Sulfur</th>
<th>Vacuum Residue Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retorted Oil</td>
<td>450</td>
<td>90.4</td>
<td>9.6</td>
<td>1.59</td>
<td>.228</td>
</tr>
<tr>
<td>ScCO$_2$</td>
<td>60</td>
<td>99.0</td>
<td>1.0</td>
<td>1.79</td>
<td>0.170</td>
</tr>
<tr>
<td>ScCO$_2$</td>
<td>160</td>
<td>72.1</td>
<td>27.9</td>
<td>1.7</td>
<td>0.374</td>
</tr>
<tr>
<td>ScCO$_2$</td>
<td>200</td>
<td>95.3</td>
<td>4.7</td>
<td>1.7</td>
<td>0.369</td>
</tr>
<tr>
<td>ScCO$_2$</td>
<td>250</td>
<td>87.2</td>
<td>12.8</td>
<td>1.75</td>
<td>0.306</td>
</tr>
</tbody>
</table>

### Oil extraction at different temperatures using ScCO$_2$

**Temperature (°C):** 60, 160, 200, 250

- **60°C**
  - Weight % of Shale: 99.0%
  - % Oil: 1.0%
  - H/C Oil: 1.79
  - % Sulfur: 0.170
  - Vacuum Residue Wt %: 16.94

- **160°C**
  - Weight % of Shale: 72.1%
  - % Oil: 27.9%
  - H/C Oil: 1.7
  - % Sulfur: 0.374
  - Vacuum Residue Wt %: 13.76

- **200°C**
  - Weight % of Shale: 95.3%
  - % Oil: 4.7%
  - H/C Oil: 1.7
  - % Sulfur: 0.369
  - Vacuum Residue Wt %: 11.56

- **250°C**
  - Weight % of Shale: 87.2%
  - % Oil: 12.8%
  - H/C Oil: 1.75
  - % Sulfur: 0.306
  - Vacuum Residue Wt %: 21.32
4. Early results

ScCO$_2$ extraction of oil from Albert oil shale with co-solvents

<table>
<thead>
<tr>
<th>Co-Solvent</th>
<th>Temperature (°C)</th>
<th>Weight % of Shale</th>
<th>% Oil</th>
<th>H/C Oil</th>
<th>% Sulfur</th>
<th>Vacuum Residue Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retorted Oil</td>
<td>450</td>
<td>90.4</td>
<td>9.6</td>
<td>1.59</td>
<td>0.228</td>
<td>43.40</td>
</tr>
<tr>
<td>THF</td>
<td>200</td>
<td>90.8</td>
<td>9.2</td>
<td>1.56</td>
<td>0.295</td>
<td>22.63</td>
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<tr>
<td>Toluene</td>
<td>200</td>
<td>90.2</td>
<td>9.8</td>
<td>1.66</td>
<td>0.400</td>
<td>11.81</td>
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<tr>
<td>Hexane</td>
<td>200</td>
<td>92.6</td>
<td>7.4</td>
<td>1.78</td>
<td>0.236</td>
<td>8.820</td>
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<td>Sc Pentane</td>
<td>200</td>
<td>90.8</td>
<td>9.2</td>
<td>1.87</td>
<td>0.290</td>
<td>15.31</td>
</tr>
<tr>
<td>ScCO2</td>
<td>200</td>
<td>95.3</td>
<td>4.7</td>
<td>1.7</td>
<td>0.369</td>
<td>11.56</td>
</tr>
</tbody>
</table>
5. Summary

+ $\text{ScCO}_2$ extraction indicates high yield oil
+ H/C ratio indicates good quality oil
+ Low residue (bitumens)
+ Change in rock properties (enhanced permeabilities if in situ?)
5. Summary

To do ($):
- Co-solvents @ 60°C
- Multiple repeats (outlier reproduction?)
- Light H-C measurements
- Before-after mineralogy (any C sequestered?)
- Different rubble (initial particle size)
- Fractured rock (core & subsurface)
- Supplemental heating of scCO₂ using microwave & sonochemical energy