Comparison of the Structure and Reactivity of an Australian Algal Coal with Jordanian and Colorado Oil Shales

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Introduction

• There is extensive background knowledge of coal liquefaction including liquefaction of the algal coal torbanite

• Currently, there is strong interest in improving methods of extracting oil from oil shale, which is derived from algae

• Aim: to establish what relationships exist between the reactivity of torbanite and typical oil shales
What are oil shale & Torbanite?

- **Oil Shale**
  - Minerals
  - Bitumen
  - Kerogen

- **Torbanite**
  - Organic solvent soluble at room temp.
  - Kerogen
Materials

• The torbanite studied is derived from freshwater algae living in the Permian period (250-300 million years ago)

• It comes from the Greta seam, New South Wales, Australia

• Ash yield 4.3 wt% db
Torbanite

- Elemental Analysis C, 82.6%, H, 10.6%, N, 0.8%, S, 0.1% O, 5.8% dmmf basis

- Atomic H/C ratio 1.53

- Mainly derived from long chain alkadienes
  \[ \text{CH}_2=\text{CH}-\left(\text{CH}_2\right)_n-\text{CH}=\text{CH}-\left(\text{CH}_2\right)_7-\text{CH}_3 \quad n= 15,17,19 \]
Jordanian oil shale

• The Jordanian oil shales studied are derived from marine algae living in the Maastrichtian age (65-70 million years ago)

• They come from El-Lajjun and Sultani (see map)

• Ash yield 75.8 wt% db (El-Lajjun), 72.3 wt% db (Sultani)

• Elemental Analysis C, 71.6%, H, 8.7%, N, 1.7%, Org. S, 9.8% O, 8.2% dmmf basis (El-Lajjun)

• Atomic H/C ratio 1.45 (El-Lajjun)

• Fe, 1.9 wt% db (El-Lajjun)
Colorado oil shale

• The Colorado oil shale is derived from lacustrine algae living in the Paleocene Epoch (55-65 million years ago)

• It comes from the Mahogany Layer, Green River formation, Colorado, above the water table (see diagram)

• Ash yield 73.2 wt% db
Rich and Lean Oil Shale Zones (Green River Formation)

Experimental Autoclave reactions

- Temperature 355-425°C
- Gas $\text{N}_2$, $\text{H}_2$, $\text{CO}$ (3 MPa cold)
- Time 1-5 hours
- Charge 2.1, 4.2 g
- 27 ml Autoclave
- Heat up time 2-4 min
- Analysis- $^1\text{H}$ NMR & GC-MS for $\text{CH}_2\text{Cl}_2$ solubles
Reaction

On-line gas analysis (including CO₂)

recover solid/liquid product with CH₂Cl₂

Lundin distillation to separate H₂O

filter

CH₂Cl₂ soluble

CH₂Cl₂ insoluble

distil off CH₂Cl₂

weigh

add n-hexane

filter

liquid

distil off n-hexane

oil

asphaltene

weigh

Desirable

Upgradable

Heat value

Inorganic Products

Hexane extraction

distil off n-hexane

weigh

add n-hexane

filter

asphaltene

liquid

oil

weigh

Useful

CH₂Cl₂ extraction

add THF

filter

THF soluble

CH₂Cl₂ insoluble

weigh

 recovery solid/liquid product with CH₂Cl₂

THF insoluble

filter

asphaltol

liquid

asphaltol

soluble

insoluble

CH₂Cl₂ extraction

GC analysis

Reaction

Heat value

Inorganic Products

Desirable

Upgradable

Useful
## Results

### Reactions of Torbanite

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Gas</th>
<th>Asphaltene</th>
<th>Oil+H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>355</td>
<td>N₂</td>
<td>0.4</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>0.3</td>
<td>3.2</td>
</tr>
<tr>
<td>390</td>
<td>N₂</td>
<td>1.1</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>1.3</td>
<td>12.7</td>
</tr>
<tr>
<td>425</td>
<td>N₂</td>
<td>12.6</td>
<td>72.4</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>13.8</td>
<td>70.3</td>
</tr>
</tbody>
</table>

Reaction for 1 hour, HC gases + CO₂ < 5%

Homogeneous structure leads to dramatic changes in reactivity with temperature
Reactions of Jordanian oil shales

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Reactant</th>
<th>Gas</th>
<th>Asphaltene</th>
<th>Oil+H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>355</td>
<td>El-Lajjun</td>
<td>N₂</td>
<td>26.8</td>
<td>33.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂</td>
<td>30.0</td>
<td>38.3</td>
</tr>
<tr>
<td></td>
<td>Sultani</td>
<td>N₂</td>
<td>19.9</td>
<td>47.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂</td>
<td>2.3</td>
<td>46.6</td>
</tr>
<tr>
<td>390</td>
<td>El-Lajjun</td>
<td>N₂</td>
<td>18.4</td>
<td>57.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂</td>
<td>9.2</td>
<td>74.7</td>
</tr>
<tr>
<td></td>
<td>Sultani</td>
<td>N₂</td>
<td>10.1</td>
<td>64.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂</td>
<td>7.8</td>
<td>59.7</td>
</tr>
<tr>
<td>425</td>
<td>El-Lajjun</td>
<td>N₂</td>
<td>4.9</td>
<td>62.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂</td>
<td>6.1</td>
<td>72.2</td>
</tr>
<tr>
<td></td>
<td>Sultani</td>
<td>N₂</td>
<td>2.8</td>
<td>74.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂</td>
<td>4.3</td>
<td>79.0</td>
</tr>
</tbody>
</table>

Reaction for 1 hour, CO₂ < 2%, little inorganic carbonate decomposition

- H₂ results usually better; maybe due to Fe catalysis
- Asphaltene to oil ratio drops significantly between 355 & 390°C
Extraction and reactions of El-Lajjun shale kerogen

- Kerogen isolated by successive extraction with 50% NaOH at 160°C followed by 5M HCl and then H₂O at room temperature
- Reaction at 390°C

<table>
<thead>
<tr>
<th></th>
<th>Gas</th>
<th>Asphaltene</th>
<th>Oil+H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td></td>
<td>15.4</td>
<td>50.4</td>
</tr>
<tr>
<td>H₂</td>
<td>14.2</td>
<td></td>
<td>46.7</td>
</tr>
</tbody>
</table>

- Conversion for N₂ reaction similar to shale but for H₂ reaction less than for shale
- Is this due to removal of Fe during kerogen extraction?
Reactions of Colorado oil shale

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Gas</th>
<th>Asphaltene</th>
<th>Oil+H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>355</td>
<td>N₂</td>
<td>2.3</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>0.6</td>
<td>12.7</td>
</tr>
<tr>
<td>390</td>
<td>N₂</td>
<td>18.5</td>
<td>31.1</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>425</td>
<td>N₂</td>
<td>11.9</td>
<td>46.3</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>13.8</td>
<td>55.4</td>
</tr>
</tbody>
</table>

Reaction for 1 hour, CO₂ yields 2-4%

- H₂ results usually better
- Significantly less reactive than Jordanian shales
Comparison of Reactivity

Reaction for 1 hour, gas N₂, hexane soluble

• Sultani > El-Lajjun > Colorado
## Elemental analysis of CH$_2$Cl$_2$ soluble material

<table>
<thead>
<tr>
<th>Shale</th>
<th>gas Charge</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O (by diff.)</th>
<th>at H/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>El-Lajjun</td>
<td>H$_2$</td>
<td>79.3</td>
<td>9.3</td>
<td>1.4</td>
<td>6.5</td>
<td>3.5</td>
<td>1.40</td>
</tr>
<tr>
<td>Sultani</td>
<td>H$_2$</td>
<td>81.0</td>
<td>10.5</td>
<td>1.3</td>
<td>3.7</td>
<td>3.5</td>
<td>1.54</td>
</tr>
<tr>
<td>Colorado 10H-C, 1440-5'</td>
<td>CO</td>
<td>82.4</td>
<td>10.3</td>
<td>2.6</td>
<td>&lt;0.3</td>
<td>4.6</td>
<td>1.50</td>
</tr>
<tr>
<td>Colorado 12H-C, 2896.1-.5'</td>
<td>CO</td>
<td>83.4</td>
<td>10.5</td>
<td>3.0</td>
<td>&lt;0.3</td>
<td>3.1</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Reaction for 1 hour, CH$_2$Cl$_2$ solubles. The O by diff. for Sultani is uncertain

- S content high for El-Lajjun
- The products from the two Colorado oil shale are similar


$^1$H NMR of CH$_2$Cl$_2$ soluble material

<table>
<thead>
<tr>
<th>Reactant</th>
<th>T °C</th>
<th>$H_{\text{ar}}$</th>
<th>$H_{\alpha}$</th>
<th>$H_{\beta}$</th>
<th>$H_{\gamma}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>El-Lajjun</td>
<td>390</td>
<td>0.09</td>
<td>0.07</td>
<td>0.53</td>
<td>0.31</td>
</tr>
<tr>
<td>Sultani</td>
<td>390</td>
<td>0.06</td>
<td>0.15</td>
<td>0.54</td>
<td>0.25</td>
</tr>
<tr>
<td>Colorado 10H-C, 1440-5'</td>
<td>425</td>
<td>0.06</td>
<td>0.16</td>
<td>0.62</td>
<td>0.16</td>
</tr>
<tr>
<td>Torbanite</td>
<td>425</td>
<td>0.07</td>
<td>0.12</td>
<td>0.68</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Reaction for 1 hour, under N$_2$, CH$_2$Cl$_2$ solubles

$H_{\text{ar}}$, 6-9 ppm; $H_{\alpha}$, 1.95-4.5 ppm; $H_{\beta}$, 1-1.95 ppm; $H_{\gamma}$, 0.5-1 ppm

- Low aromatic content
- High $H_{\beta}$ signifying long aliphatic chains
GC-MS of $\text{CH}_2\text{Cl}_2$ soluble material

**El-Lajjun**

**Sultani**

**Col 12H-C May #4 chunks**

**Torbanite**

Reaction for 1 hour, under $\text{N}_2$, $\text{CH}_2\text{Cl}_2$ solubles

- Note close similarity between Colorado and torbanite
- Jordanian oil shales similar to each other despite difference in S content but very different to Colorado & Torbanite
## Extended reaction time at 390°C

<table>
<thead>
<tr>
<th>Shale</th>
<th>Conversion wt% dmmf</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1h</td>
</tr>
<tr>
<td>El-Lajjun</td>
<td>78.5</td>
</tr>
<tr>
<td>El-Lajjun (355°C)</td>
<td>61.2</td>
</tr>
<tr>
<td>Colorado 10H-C, 1440-5'</td>
<td>51.1</td>
</tr>
<tr>
<td>Torbanite</td>
<td>14.8</td>
</tr>
</tbody>
</table>

Reaction under N₂, CH₂Cl₂ solubles

- Torbanite and Colorado conversion increase markedly from 390-425°C and with reaction time
- El-Lajjun conversion does not increase with reaction time
Summary

• The freshwater algal coal Torbanite and lacustrine Colorado oil shale react more slowly than the marine Jordanian oil shales (El-Lajjun and Sultani).

• Products from materials of non-marine algal origin are remarkably similar even though there is a 200 million year difference in age.

• The products from the Jordanian shales are more complex due in part to the large number of S compounds.

• No direct correlation between organic S content of the shales and the reactivity, Sultani, with significantly less S, reacting more readily than El-Lajjun.
Acknowledgments

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