Post Retort Pre Hydro-treat Upgrading of Shale Oil

M. Karanjikar, J. Alvare, D. Chitta, D. Larsen, J. Gordon
Ceramatec Inc
2425 South 900 West
Salt Lake City UT 84119
801 972 2455
www.ceramatec.com

Presented at the 30th Oil Shale Symposium, Golden, CO
Shale Oil Value Chain

- Surface Retort (e.g. Paraho, ATP)
- In-situ Retort (e.g. Shell, ExxonMobil)

Production of Oil

- Removal of Sulfur, Nitrogen and Heavy Metals
- Enhancing the API value

Ceramatec Upgrading Process

Refining

- Gasoline
- Jet Fuel
- Diesel
- Chemicals
Ceramatec Overview

- Privately Owned
- Founded 1976
- Subsidiary Company of CoorsTek
  - CoorsTek very large tech ceramic manufacturer & 100 year old U.S. company
- 140,000 ft² R&D and Mfg Facility
- Concept to commercialization
  - R&D --> prototype --> pilot scale fabrication -->
- Core competencies
  - electrochemistry, ionic conducting ceramics, & advanced materials
- Customers
  - 60% Fortune 100/500 Companies
  - 40% Government
Shale Oil Upgrading Technology Objectives

- Remove nitrogen, sulfur, & metals
  - Without saturating organics
    - Avoid octane loss
  - Without coking
    - Maximize product output
- Upgrade with controlled level of hydrogenation
- Bring shale oil to levels acceptable to refineries
Overall Upgrading Process

Demonstrate with Reactor

Shale oil \rightarrow \text{Reaction} \rightarrow \text{Separation} \rightarrow \text{Electrolysis} \rightarrow \text{Sulfur} \rightarrow \text{Metals} \rightarrow \text{Upgraded oil}

- Hydrogen (H₂)
- Ammonia (NH₃)
- Oil + Salt
- Sulfur (H₂S)
- Metals
- Electric Power
- Make-up alkali metal (Li or Na)
- Recycle

CERAMATEC
Tomorrow's Ceramic Systems
Background

Alkali metal treatment of heavy petroleum crude known since ’70s

<table>
<thead>
<tr>
<th>U.S. PAT.</th>
<th>YEAR</th>
<th>PATENT TITLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,076,613</td>
<td>1978</td>
<td>Comb. Desulf. and Conversion with Alkali Metals</td>
</tr>
<tr>
<td>5,695,632</td>
<td>1997</td>
<td>Cont. In-Situ Comb. Proc for Upgrading Heavy Oil</td>
</tr>
<tr>
<td>5,935,421</td>
<td>1999</td>
<td>Cont. In-Situ Comb. Proc for Upgrading Heavy Oil</td>
</tr>
<tr>
<td>6,210,564</td>
<td>2001</td>
<td>Proc. for Desulf. of Pet. Feeds Utilizing Sodium Metal</td>
</tr>
</tbody>
</table>
## Literature Examples

<table>
<thead>
<tr>
<th>Reactor Conditions</th>
<th>Safaniya atm. R</th>
<th>Safaniya vac. R.</th>
<th>Bitumen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time minutes</td>
<td>25</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Temp C</td>
<td>443</td>
<td>438</td>
<td>438</td>
</tr>
<tr>
<td>H2 Press psig</td>
<td>1400</td>
<td>2000</td>
<td>1675</td>
</tr>
<tr>
<td>Na/S Atom ratio</td>
<td>2.6</td>
<td>2.2</td>
<td>2.5</td>
</tr>
<tr>
<td>H2 Used, SCF/B</td>
<td>365</td>
<td>500</td>
<td>570</td>
</tr>
</tbody>
</table>

### Results

<table>
<thead>
<tr>
<th></th>
<th>In</th>
<th>Out</th>
<th>In</th>
<th>Out</th>
<th>In</th>
<th>Out</th>
</tr>
</thead>
<tbody>
<tr>
<td>API Gravity</td>
<td>14.4</td>
<td>26.2</td>
<td>4.6</td>
<td>21.6</td>
<td>10.3</td>
<td>24.8</td>
</tr>
<tr>
<td>Sulfur Wt%</td>
<td>3.91</td>
<td>0.07</td>
<td>5.2</td>
<td>0.3</td>
<td>4.49</td>
<td>0.4</td>
</tr>
<tr>
<td>Nitrogen Wt%</td>
<td>0.26</td>
<td>0.1</td>
<td>5.2</td>
<td>0.3</td>
<td>4.49</td>
<td>0.4</td>
</tr>
<tr>
<td>Conrad Carbon Wt%</td>
<td>11.8</td>
<td>1.35</td>
<td>23.7</td>
<td>14.9</td>
<td>12.3</td>
<td>5.6</td>
</tr>
<tr>
<td>Na Efficiency</td>
<td>76%</td>
<td></td>
<td>86%</td>
<td></td>
<td>73%</td>
<td></td>
</tr>
</tbody>
</table>

US patent #. 4,076,613
Chemistry

Initial reaction with alkaline metal ~375 °C, 1000psi
- \( R - S - R' + 2Na + H_2 \rightarrow R-H + R'-'H + Na_2S \)
- \( R, R', R''-N + 3Na + 1.5H_2 \rightarrow R-H + R'-'H + R''-'H+ Na_3N \)
- Heavy metals are reduced by Na

Formation of salt phase for separation
- \( Na_2S + H_2S \rightarrow 2NaHS \) (liquid at 375 °C)
- \( Na_3N + 3H_2S \rightarrow 3NaHS + NH_3 \)
- Vent and recover ammonia

Treatment of alkali hydrosulfide with polysulfide
- \( 2NaHS + Na_2S_x \rightarrow H_2S + 2Na_2S_{(x+1)/2} \)
- Recycle hydrogen sulfide back to reactor for forming salt phase

Electrolysis
- Reduce Alkali metal, upgrade low polysulfide to high polysulfide
- Cathode: \( Na^+ + e^- \rightarrow Na \)
- Anode: \( (1) Na_2S_x \rightarrow Na^+ + e^- + \frac{1}{2} Na_2S_{(2x)} \)
  \( (2) Na_2S_x \rightarrow Na^+ + e^- + \frac{1}{2} Na_2S_x + x/16 S_8 \)

Sulfur removal
## Reactor Demonstration - Experimental

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>heavy Crude(HC), Shale Oil 1(SO-1) and Shale Oil 2 (SO-2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>275 – 375 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>~ 1000 psi</td>
</tr>
<tr>
<td>Na/Li to S or N Ratio</td>
<td>Stoichiometric</td>
</tr>
<tr>
<td>Time</td>
<td>1 Hr</td>
</tr>
<tr>
<td>Analysis</td>
<td>Simdist and CHNS</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>C (%)</th>
<th>H(%)</th>
<th>N (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO-1</td>
<td>85.48</td>
<td>12.33</td>
<td>1.48</td>
<td>0.25</td>
</tr>
<tr>
<td>SO-2</td>
<td>84.83</td>
<td>12.74</td>
<td>0.47</td>
<td>0.84</td>
</tr>
<tr>
<td>HC</td>
<td>85.70</td>
<td>11.27</td>
<td>0.76</td>
<td>1.54</td>
</tr>
</tbody>
</table>
# Results (Early)

<table>
<thead>
<tr>
<th>Experiment (Na)</th>
<th>C (%)</th>
<th>H(%)</th>
<th>N (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (SO-1)</td>
<td>85.79</td>
<td>12.97</td>
<td>0.72</td>
<td>0.04</td>
</tr>
<tr>
<td>2 (SO-2)</td>
<td>85.77</td>
<td>12.99</td>
<td>0.39</td>
<td>0.51</td>
</tr>
<tr>
<td>3 (HC)</td>
<td>85.61</td>
<td>11.51</td>
<td>0.77</td>
<td>0.37</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experiment (Li)</th>
<th>C (%)</th>
<th>H(%)</th>
<th>N (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (SO-1)</td>
<td>85.15</td>
<td>12.49</td>
<td>1.23</td>
<td>0.1</td>
</tr>
<tr>
<td>2 (SO-2)</td>
<td>85.36</td>
<td>12.69</td>
<td>0.38</td>
<td>0.4</td>
</tr>
<tr>
<td>3 (HC)</td>
<td>85.38</td>
<td>11.32</td>
<td>0.72</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Sulfur Reduction**
- Na: 84% (SO-1), 40% (SO-2), 75% (HC)
- Li: 60% (SO-1), 52% (SO-2), 16% (HC)

**Nitrogen Reduction**
- Na: 51% (SO-1), 17% (SO-2)
- Li: 17% (SO-1), 23% (SO-2)

**SimDist**
- 41 °C reduction in BP at 60% boil-off (HC)
- 65 °C reduction in BP at 60% boil-off (HC)
Conclusion

- Sulfur and Nitrogen are removed effectively from shale oil
- Results obtained from Na are more promising for shale oil feedstock
- Electrochemical Recovery of alkali metal has been demonstrated
Work-in-Progress and Way Forward

- Further process optimization
- Continuous process
- Effective continuous separation of polysulfides from oil phase
- Efficient recovery of alkali metal
- Scale-up to a pilot level

Collaboration Opportunities

**Bench Scale**
- Started in 2009
- 6 months to transition

**Optimization**
- Until late 2011
- Continuous process
- Precise economics

**Pilot**
- Commercial Partners
- Offsite or Field Demonstration
Acknowledgement

We acknowledge the financial support from the Department of Energy.
Contact
John Gordon
Manager - Upgrading Development
801-978-2138
johng@ceramatec.com

Contact
Anthony Nickens, Vice-president
Ceramatec Inc,
2425 South 900 West,
Salt Lake City, Utah 84119
801 – 978 – 2113
anickens@ceramatec.com