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Sim Romero, Principal Consultant for KBC Advanced Technologies, Inc., has over 30 years experience in Heavy Oil Processing, and he is a specialist in Delayed Coking. Mr. Romero has worked in the area of delayed coking for several major oil companies (ConocoPhillips, BP Oil, ARCO, ExxonMobil and Valero), where he directed numerous expansion and optimization programs. As the Delayed Coking Technical Manager at Bechtel, he oversaw the construction of four grass roots delayed coker units. Mr. Romero’s expertise ranges from heavy oil thermal kinetic model development to startup, trouble shooting and general operations of delayed coker units.

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Comparison of Thermal Cracking and Hydro-Cracking Yield Distributions

Sim Romero and Scott Sayles
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Bitumen upgrading is challenging. In the current economic climate operators of upgraders are faced with obtaining the maximum performance from existing equipment. The existing equipment is typically operating at the upper end of the design envelope and performance is pushed to the limits of the constraining equipment. The typical major constraint is the primary upgrader processes, coking or hydrocracking. Funding for new equipment to remove the constraints is difficult to obtain at the current time and economic conditions. However, by understanding of the fundamental kinetics in thermal cracking and hydrocracking provides insights into the operational changes that can be made to optimize unit performance.

This paper will briefly review the yield distribution differences between thermal cracking and hydrocackling. The goal is to compare yields, product quality distributions and the elemental balances. Once these basic components to the unit operation are understood, the opportunities to increase production and improve performance can be analyzed quantitatively within the existing unit equipment limits.
Comparison of Thermal Cracking and Hydro-Cracking Yield Distributions

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• Kinetics in thermal cracking and hydrocracker
• Yields comparison
• Carbon and hydrogen balance
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Introduction

- Goals is to obtain the maximum performance from existing equipment.
- Existing equipment is typically:
  - Operating at the upper end of the design envelope
  - Performance is pushed to the limits of the constraining equipment.
  - Typical major constraints are the primary upgrader processes:
    - coking or hydrocracking.
  - Funding for new equipment to remove the constraints is difficult to obtain at the current time and economic conditions.
- Understanding of the fundamental kinetics in thermal cracking and hydrocracking provides insights into the operational changes that can be made to optimize unit performance.
Generic Coker

- Delayed Coker Reactions Consist of Cracking and Polymerization
KBC Kinetic Model: RDS-SIM

- Design Screen from DC-SIM
KBC Kinetic Model: RDS-SIM

- Design Screen from RDS-SIM
Kinetics

• Conversion

  – Both coking and hydrocracking use thermal cracking to convert residua
  – Hydrocracking injects hydrogen which short circuits the polymerization or condensation reactions – hydrogen approach
  – Delayed Coking allows polymerization or condensation – a carbon rejection approach
Kinetics: Hetro-Atom Removal

- Downflow Desulfurization Example
  - Oil and gas residence times
  - Catalyst activity varies with time

- Catalyst deactivation increases due to feed contaminants
- HDS is a function of catalyst activity
Yield Comparison: Basis

- **Feedstock**
  - Typical Athabasca Bitumen
  - SAGD produced
  - Diluent Removed
  - Bitumen is cut first in a Vacuum Unit

<table>
<thead>
<tr>
<th>Description</th>
<th>Units</th>
<th>Bitumen</th>
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<tbody>
<tr>
<td>Production Method</td>
<td></td>
<td>SAGD</td>
</tr>
<tr>
<td>% Diluent in Blend</td>
<td>v%</td>
<td>0</td>
</tr>
<tr>
<td>% Diluent in Blend</td>
<td>w%</td>
<td></td>
</tr>
<tr>
<td>API</td>
<td></td>
<td>9.0</td>
</tr>
<tr>
<td>Elemental Analysis, Dry</td>
<td>w%</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>84.1</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>10.0</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>4.6</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td>0.4</td>
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<tr>
<td>Metals</td>
<td>wppm</td>
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</tr>
<tr>
<td>Ni</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td>170</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td>300</td>
</tr>
<tr>
<td>Oxygen</td>
<td>w%</td>
<td>0.8</td>
</tr>
<tr>
<td>Total</td>
<td>w%</td>
<td>100.0</td>
</tr>
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</table>
Yield Comparison: Basis

• Assumed a unit feed from a Vacuum Unit
  – 1,020°F residue cut point

<table>
<thead>
<tr>
<th></th>
<th>Whole Bitumen</th>
<th>Gas Oil</th>
<th>Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol%</td>
<td>100.00%</td>
<td>47.72%</td>
<td>52.28%</td>
</tr>
<tr>
<td>API</td>
<td>9.00</td>
<td>16.37</td>
<td>2.88</td>
</tr>
<tr>
<td>UOP K</td>
<td>11.33</td>
<td>11.40</td>
<td>11.27</td>
</tr>
<tr>
<td>MW</td>
<td>527</td>
<td>384</td>
<td>763</td>
</tr>
<tr>
<td>C/H wt</td>
<td>8.70</td>
<td>8.02</td>
<td>9.26</td>
</tr>
<tr>
<td>Sulfur Wt%</td>
<td>4.60%</td>
<td>3.45%</td>
<td>5.55%</td>
</tr>
<tr>
<td>Nitrogen, ppm</td>
<td>4,000</td>
<td>2,299</td>
<td>4,756</td>
</tr>
<tr>
<td>MCC wt%</td>
<td>14.5%</td>
<td>1.1%</td>
<td>25.7%</td>
</tr>
<tr>
<td>Metals, ppm</td>
<td>530</td>
<td>207.75</td>
<td>776</td>
</tr>
</tbody>
</table>

• Operations
  – 100 KBPD
  – Coker + Equipment to make same sulfur as Hydrocracker
  – Ebullated Bed Hydrocracker + H2 plant
Yield Comparison: Basis

- **Coking**
  - Severe Thermal Conversion
  - Coker Drum in multiple pairs (i.e. 100,000 BPD unit will have 6 drums or 3 modules)
  - Target a 4 to 5 year run length with slowdowns for heater cleaning

- **Hydrocracking**
  - Moderate Conversion
  - Ebullated Bed, three reactors
  - Catalyst Addition
  - Target a three year run length
A mass comparison shows the yields are very similar.
Sulfur Balance

In the Delayed Coker, sulfur mostly reports to the coke and H2S.

Liquid products have ~25% of the total sulfur.

In the Hydrocracker, sulfur mostly reports to H2S for obvious reasons.

Products have very little sulfur - liquid products (C5 to 1000°F) have ~5% of the total sulfur.
Nitrogen mostly reports to the coke because nitrogen is concentrated in the asphaltenes and are difficult to hydrotreat.

Nitrogen removal in the form of NH3 is significant in the hydrocracker.

Liquid products have far less nitrogen.

Nitrogen mostly reports to the residual bottoms product. Nitrogen is concentrated in the asphaltenes and are difficult to hydrotreat.

Relatively small amounts of NH3 because there is no hydrotreating or free hydrogen reactions.

Nitrogen content is higher in the liquid products (approximately twice the hydrocracker).
Carbon and Hydrogen

- The Delayed Coker is a carbon rejection process
- Liquid products are still rich in carbon and are generally aromatic

- The Hydrocracker is a hydrogen in process but the carbon is still rejected to the heavy residual stream
- Carbon rejection (1000°F plus stream) is a function of conversion and catalyst life
Carbon and Hydrogen

- The Delayed Coker is a carbon rejection process with a high concentration of carbon leaving with the coke.
- The hydrocracker injects hydrogen into the balance and both saturates the residual bottoms and removes sulfur and nitrogen from the liquid products.
Yield Comparison Summary

- The hydrocracker yields are much less aromatic and have been hydrotreated.
- Coker products have reduced sulfur and nitrogen levels with the coke receiving a large portion of the contaminants - despite the lack of hydrogen and active removal of sulfur and nitrogen.

<table>
<thead>
<tr>
<th>Liquid Products</th>
<th>Delayed Coker</th>
<th>Hydrocracker</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>API Gravity</td>
<td>Wt% Sulfur</td>
</tr>
<tr>
<td>Naphtha (c5 - 400°F)</td>
<td>62.5</td>
<td>0.5%</td>
</tr>
<tr>
<td>LCGO (400-650°F)</td>
<td>28.3</td>
<td>2.1%</td>
</tr>
<tr>
<td>HCGO (650°F plus)</td>
<td>13.5</td>
<td>3.7%</td>
</tr>
<tr>
<td>1000°F plus residual</td>
<td>N/A</td>
<td>8.8%</td>
</tr>
</tbody>
</table>
Conclusions

- Delayed Coking and Hydrocracking are not competing processes
  - Most heavy oil streams must undergo multiple steps to produce finished products
  - The economics favor a multi-step process
  - Capitalize on the strengths of both processes
Conclusions

• Other issues can play in the analysis and economics
  – Conversion in the hydrotreater
  – Availability of hydrogen
  – Coke disposal – market value
  – Product margins (diesel vs. gasoline market)

• Selection of the process needed for a given refinery configuration is site specific and KBC can help.
Questions?