Hydrocracking of Deasphalted Oil

IMP/Pemex Refinacion
Refining Technology Seminar
September 6, 2006
Agenda

◆ Hydroprocessing Role in Upgrading
◆ DAO Hydrocracking
  ▪ Why DAO Hydrocracking?
  ▪ Lab Data and Catalyst evaluation (Fuels and Lubes)
  ▪ Advanced Reactor Design
    ▪ Spider Vortex Internals
    ▪ Automatic Bed By-pass
◆ Conclusions
EMRE Technologies for Quality Fuels

EMRE HYDROFINING

Naphtha
- FCC Naphtha
- SCANfining
- OCTGAIN
- Hydrofining

Distillate
- ULSD
- ULSD + MAXSAT
- ULSD + HDHDC

Waxy Feeds
- MDDW
- MIDW

Heavy Feeds
- MPHC (+PTU)
- GOfining
- RESIDfining
- MPHC + MIDW
- LCO Upgrading
Resid Quality Drives Conversion Options

- **Very Low CCR/Metals**
  - Once through Hydrocracking
- **Low CCR/Low Metals**
  - Resid FCC possible
- **Mid CCR/Mid Metals**
  - Utilize hydroprocessing to upgrade slate
    - + ARDS
    - + LC-Fining/H-Oil
    - + Microcat-RC
- **High CCR/High Metals**
  - Reject carbon to coke product- FXK, DLK
  - Segregate hydrogen to liquids/gas
  - ROSE allows a % of high CCR/High metals to HP or Resid FCC applications and reduce the size of the coker
Removing Asphaltene from Resid

- Removes CCR
- Removes Metals
- Removes Polars (i.e. sulfur, nitrogen)
- Reduces viscosity
- DAO becomes viable HDC feedstock
- FJK or DLK unit is smaller capacity
Typical Contaminant Distribution in ROSE DAO

% COMPONENT IN DAO

DAO YIELD, VOL %

SULFUR
NITROGEN
METALS
CCR
ASPHaltenES
Flow Diagram For DAO Hydrocracking

- VGO/DAO
- Hydrogen Feed
- Steam
- Recycle Compressor
- Lean Amine
- Rich Amine
- Off-Gas
- High Temp. Separator
- Low Temp. Separator
- Stripper
- Fractionator
- Gasoline
- Naphtha
- Kerosene
- Diesel
- Steam
- Waxy Basestocks or FCC Feed
HDC Reaction Zones

Reactor Configuration

Catalyst Type

HDC Reactions

Treating Zone

Metal

Cracking Zone

Bifunctional (Metal + Acid)

Post Treat Zone

Metal

HDM

HDS

HDN

HDN

selective cracking with low arosat

Sulfur polishing If needed

Bitumen Derived DAO

Example HP Pilot Plant Studies at EMRE
ROSE and Hydrotreating Study

Feed

• DAO Source – Solvent extraction of 650+ Alberta bitumen

• DAO Quality
  - API Gravity 14.4
  - Sulfur, wt% 3.5
  - Nitrogen, wt% 0.20
  - Vanadium, ppmw 12
  - Nickel, ppmw 6
  - ConCarbon, wt% 3.3
  - C5 Insolubles, ppmw 100

• Laboratory Tests on Bitumen Derived DAO
  • Parallel sets of tests with two catalysts
  • Product yield and quality
# Bitumen DAO Hydrotreating

## Test Results – Bitumen Feed

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th>Light DAO Catalyst A</th>
<th>Light DAO Catalyst B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure, psig</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>Temperature, F</td>
<td>700</td>
<td>700</td>
</tr>
<tr>
<td>LHSV, 1/hr</td>
<td>0.62</td>
<td>0.62</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Treated Product Quality</th>
<th>Light DAO Catalyst A</th>
<th>Light DAO Catalyst B</th>
</tr>
</thead>
<tbody>
<tr>
<td>API Gravity</td>
<td>25.1</td>
<td>26.2</td>
</tr>
<tr>
<td>Sulfur, wt%</td>
<td>481</td>
<td>145</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>359</td>
<td>63</td>
</tr>
</tbody>
</table>
DAO Hydrocracking

Example HP Pilot Plant Studies at EMRE
Pilot Plant Study
DAO Partial Conversion Hydrocracking

• Feed: 30/70 blend of DAO/VGO
• MPHC Feed quality
  – API 22.2
  – Sulfur 1.42 w%
  – Nitrogen 1300 ppmw
  – RI@70C 1.491
  – Ni+V, ppmw 5.8
  – SimDis 10/90% 692/11171F
  – CCR ~2 wt%
• Conversion 13-60%
• With DAO/VGO feeds yields similar to VGO only except increased hydrogen use
# DAO HDC Pilot Study

## Operating Conditions and Yields on 30/70 DAO/VGO

- **Pressure, psig**: 1,960
- **H₂ Circulation, SCF/BBL**: 6,000

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Base</th>
<th>Base + 25</th>
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</thead>
<tbody>
<tr>
<td>650 F+ Conversion</td>
<td>13</td>
<td>53</td>
</tr>
<tr>
<td>H₂ Consumption</td>
<td>825</td>
<td>1530</td>
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</table>

<table>
<thead>
<tr>
<th>Yields, Vol%</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C5-180 F</td>
<td>0.2</td>
<td>7.2</td>
</tr>
<tr>
<td>180-330 F</td>
<td>1.8</td>
<td>17.0</td>
</tr>
<tr>
<td>330-440 F</td>
<td>2.1</td>
<td>17.8</td>
</tr>
<tr>
<td>440-650 F</td>
<td>12.5</td>
<td>22.1</td>
</tr>
<tr>
<td>650 F+</td>
<td>87.2</td>
<td>47.5</td>
</tr>
</tbody>
</table>
# DAO HDC Pilot Study

## Product Qualities for 53% Conversion

<table>
<thead>
<tr>
<th></th>
<th>Lt. Naphtha</th>
<th>Hvy. Naphtha</th>
<th>Kero.</th>
<th>Diesel</th>
<th>FCCU Feed</th>
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<tbody>
<tr>
<td>Gravity</td>
<td>80</td>
<td>53</td>
<td>44.1</td>
<td>40.2</td>
<td>35.1</td>
</tr>
<tr>
<td>Sulfur, ppmw</td>
<td>&lt;10</td>
<td>&lt;100</td>
<td>&lt;200</td>
<td>&lt;200</td>
<td>&lt;200</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;1.0</td>
<td>&lt;5</td>
</tr>
<tr>
<td>RON Clear</td>
<td>77</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smoke</td>
<td></td>
<td></td>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cetane Index</td>
<td></td>
<td></td>
<td>40</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>Ni+V, ppmw</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt;0.3</td>
</tr>
</tbody>
</table>
HDC DAO for Lubes

• High Viscosity of HDC DAO bottoms can be a potential lubes feedstock
  • VI must be increased to meet lube specifications (related to conversion)
  • Sulfur and nitrogen must be reduced sufficiently to allow hydroisomerization
• ExxonMobil Licenses such a hydroisomerization process (MSDW) with 16 Licensees. Some process HDC and HDT DAO.
## HDC DAO for Lubes using MSDW

Results of 6 month pilot study with 2 different DAO feeds

<table>
<thead>
<tr>
<th>Feed#</th>
<th>HDC severity</th>
<th>MSDW Feed</th>
<th>MSDW Product (bottoms fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DAO A</td>
<td>DAO B</td>
<td>Nitrogen, ppmw</td>
</tr>
<tr>
<td>1</td>
<td>high</td>
<td>2</td>
<td>low</td>
</tr>
<tr>
<td>1</td>
<td>high</td>
<td>2</td>
<td>low</td>
</tr>
<tr>
<td>8</td>
<td>24</td>
<td>283</td>
<td>146</td>
</tr>
<tr>
<td>0.01</td>
<td>0.06</td>
<td>0.14</td>
<td>0.57</td>
</tr>
<tr>
<td>20.7</td>
<td>28.9</td>
<td>24.1</td>
<td>40.1</td>
</tr>
<tr>
<td>120</td>
<td>100</td>
<td>107</td>
<td>93</td>
</tr>
<tr>
<td>-14</td>
<td>-11</td>
<td>-2</td>
<td>-8</td>
</tr>
</tbody>
</table>
Reactor Internals Design
Importance of Reactor Design

- Internal design is more and more critical for higher conversion/ more stringent product specifications
  - low sulfur specs unforgiving for any maldistribution
  - lower radial delta T minimizes peak temperature and gives longer life

**Solution:**
*ExxonMobil Spider-Vortex*
Automatic Bed Bypass Technology: Simple and Effective

- Proprietary design enables automatic bypassing of flows around fouled catalyst layer
- Simple, low-cost construction
- Automatic operation with no moving parts
- Protects against unavoidable bed fouling events by “buying time”
Conclusions

• DAO Hydrocracking – an EMRE technology based on understanding of fundamentals and backed by extensive development and operating experience

• DAO is an effective HDC Feedstock for single pass hydrocracking units

• Bottoms products make excellent FCC feed

• Making 10 ppm diesel from DAO is possible but a post treat unit is preferred to maintain performance

• HDC DAO bottoms can make excellent lubes with <10 ppm sulfur product diesel possible when processing over MSDW.
Back up
Materials with Complex Structures

- **Asphaltenes**
  Precipitated from Crude Oils by Aliphatic Solvents (e.g. n-C\textsubscript{5}). Soluble in Benzene. Mol. Wt. 1000-3000. High in S, N, O, and Metals (V + Ni).

C\textsubscript{84}H\textsubscript{98}N\textsubscript{2}S\textsubscript{2}O\textsubscript{3}
1248 Mol. Wt.
40.4% Aromatic Carbons

- 80.85 wt\%C
- 7.92 wt\%H
- 2.24 wt\%N
- 5.14 wt\%S
- 3.85 wt\%O