New hydrocracking catalyst brings higher diesel yield and increases refiner’s profitability

Criterion Catalysts & Technologies
Zeolyst International

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GM Hydrocracking

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Outline

- Hydrocracking Adds Value
- Advances in Zeolite and Catalyst Technology
- The Hydrocracker at Shell Pernis Refinery
- Z-FX10 Development
- Commercial Performance
Hydrocracker margin

- Margin is created by upgrading relatively low value feedstocks into high value clean products
- Low value feedstocks, e.g.:
  - Heavy VGO
  - Heavy Coker Gas Oil
  - Heavy Cycle Oil
  - De-asphalted Oil
- High value products, e.g.:
  - Middle distillates (Euro V Diesel, jet A-1 kero)
  - Naphtha (gasoline blending stock)
  - Unconverted oil (for lubes or chemical feedstock)

Middle Distillates market is growing worldwide and sets the direction for hydrocracker operation and catalyst development.
Right catalysts are Key to improve hydrocracker margins

- Poison guards, HDM and HDCCCR catalysts protect hydrotreating downstream, to secure desired cycle length.

- HDS/HDN high activity and high stability pretreat catalyst provide low nitrogen and aromatics slip to the zeolitic hydrocracking catalyst.

- Selective and active cracking catalysts will give a high yield in middle distillate at designed cycle length.
Fundamental Understanding Improves Manufacturing

Electron microscopy
Bulk structure

Increased homogeneity

SEM/EDX
Chemical structure

SAR

Dialog with Manufacturing
Equivalent Activity with Less Zeolite Allows Room for Other Material

New Zeolite
- Higher purity
- Improved product selectivity
- More activity

Extra Room
- Extra room for hydrogenation (or other zeolitic functions)
- Better HDS, HDN, and HDA
Advanced Trilobe eXtra (ATX) Shape

TL Trilobe Shape

New ATX Trilobe Shape
- Advanced Trilobe eXtra
- Improves Diffusion
- Larger void fraction gives better pickup of particulates
- SOR $\Delta P$ for ATX is 25% less than the SOR $\Delta P$ for TL
- Available for most Criterion/Zeolyst hydrocracking catalysts
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The Pernis Hydrocracker in Summary

- Single stage once through
- Shell Global Solutions design
- High conversion

Feed:
- HS VGO
- TCFD
- HCO
- Extracts

Objectives:
- Maximum Jet A-1 and ULSD
- Minimum hydrogen consumption
- Good quality ethylene cracker feed
How HCU Performance Impacts Downstream Units

- HS VGO, TCFD, Extracts HCO,
- C4, Naphtha, Jet A-1, ULSD
- Naphtha, LPG
- Moerdijk steamcracker
- MLO products
- CC2 products

- Hydrowax
Right balance between units to optimize Enterprise Economics

<table>
<thead>
<tr>
<th>Pernis HCU</th>
<th>Moerdijk steamcracker</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Catalyst cycle length</td>
<td>• Hydrowax quality:</td>
</tr>
<tr>
<td>• Level of conversion</td>
<td>- Ethylene yield,</td>
</tr>
<tr>
<td>• Maximizing middle distillate yield</td>
<td>- Furnace run length,</td>
</tr>
<tr>
<td></td>
<td>- Pitch yield.</td>
</tr>
</tbody>
</table>

Hydrowax hydrogen content is a key parameter for oil/chemical interface and thus for the HCU catalyst selection.
Outline

● Introducing Criterion/Zeolyst Hydrocracking Catalysts
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2004 Challenge: produce 10 ppm sulfur HCU gasoil
- Cracking: more active V-USY zeolite and higher HDS activity.
- Pretreat: more balanced HDS and HDN functions.

2008 Challenge: Increase HCU Middle Distillate yields
- Cracking: more active and selective D-VUSY zeolite allowed addition of other functions.
- Pretreat: improved demetallization function for heavier feeds.
Drivers for development Z-FX10

- 2012 Challenge:
  - Increase Middle Distillate yield.
  - Maintain Hydrowax quality.
2012 Development for Pernis: Z-FX10

- Z-2723: MD
  - Excellent cold flow
- Z-FX10: MD
  - Enhanced cetane
- Z-3xxx: HDA
  - HDS

Middle distillates selectivity vs. Cracking activity

- Classic
- State of the art
- New step-out portfolio
Pilot plant results: Z-FX10 increases middle distillates selectivity by 3–4wt%.

<table>
<thead>
<tr>
<th></th>
<th>Z-3723</th>
<th>Z-FX10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>Canadian synthetic VGO (ring rich)</td>
<td>HVGO</td>
</tr>
<tr>
<td>Middle distillate selectivity, %</td>
<td>Base</td>
<td><strong>Base +4</strong></td>
</tr>
<tr>
<td>Diesel cetane</td>
<td>Base</td>
<td><strong>Base +1</strong></td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Feed Properties</th>
<th>HVGO blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity @ 15°C</td>
<td>0.9</td>
</tr>
<tr>
<td>Sulphur, %wt</td>
<td>2.4</td>
</tr>
<tr>
<td>Nitrogen, ppmw</td>
<td>1500</td>
</tr>
<tr>
<td>Conradson carbon, %wt</td>
<td>0.7</td>
</tr>
<tr>
<td>&gt;540°C, %wt</td>
<td>10</td>
</tr>
<tr>
<td>T95%, °C</td>
<td>570</td>
</tr>
</tbody>
</table>
Commercial Operation Confirms Yields Benefits
Conclusion
Commercial Operation also Confirms

- 3.8 % woff higher Middle Distillate yield.
- Similar Hydrogen consumption as Z-3723.
- Similar Hydrowax Hydrogen content as Z-3723.

Application of Z-FX10 resulted for Oil/Chemical integration economics: an annual margin improvement of $>5\text{ M}$
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