Exceptional Stability through High Performance Hydroprocessing (HPC) Catalysts

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Agenda

• Function of HPC Catalysts
• Composition of HPC Catalysts
• Catalyst Technology Development
• Importance of Stability
• Examples of Activity & Stability improvements
Function of HPC Catalysts

• Purification of Petroleum Fractions (Hydrotreating):
  • Removal of S & N reduces pollution from gasoline & diesel
  • Saturation of aromatics improves Smoke point of jet and Cetane quality of diesel
  • Remove contaminants and inhibitors from feeds to downstream refinery processes such as FCC, reforming, etc.

• Conversion of Higher Boiling Molecules (Hydrocracking):
  • Isomerize long straight chain paraffins into branched paraffins to improve cold flow properties
  • Crack large molecules (680 °F plus) into smaller ones to be used as fuel or Lube oil base stocks

• As the name implies, these reactions occur in the presence of H₂ at elevated temperature and pressure
Composition of HPC Catalysts

- **Hydrogenation Function:**
  - Made up of high activity metal sulfides such as Ni, Co, Mo (base metal) or Pt, Pd (noble metal)

- **Cracking Function:**
  - Provided by amorphous oxides (Alumina, Silica-Alumina) or by crystalline zeolites.
  - Ratio of cracking and hydrogenation functions is critical to optimize activity and selectivity.

- **Binder (Alumina):**
  - High surface area enabling good dispersion of active phase
  - High void fraction to enable easy access to active sites
  - Minimal activity to prevent undesirable reactions and good strength to avoid breakage

- Hydrocracking catalysts are bifunctional in nature and include hydrogenation & cracking activity
Catalyst Technology Development

- **GOLD CENTERA**: DC-2618, DN-3630 (2009), DC-2635 (2013)
- **CENTERA**: DC-2318, DN-3330 (2006), DC-2534 (2011)

- **2000**: DC-2118, DN-3110
- **2004**: DC-2531
- **2006**: DC-2318, DN-3330
- **2009**: DC-2618, DN-3630
- **2011**: DC-2534
- **2013**: DC-2635
- **2014**: DC-2533, DN-3531, DN-3532

**Arab Medium SR Diesel 300 psig**

- DC-2531
- DC-2618
- DC-2635

10-25°F Activity Benefit

**US Cracked Feed 1200 psig**

- DN-3531
- DN-3630
- DN-3636

10-25°F Activity Benefit
Importance of Stability

• While activity gain is critical in catalyst development, truly successful performance combines good activity with low deactivation rate to enable either longer life or improved ability to process more difficult feeds.

• Higher hydrogenation activity means lower propensity to form coke.

• Physical properties of the binder play a critical role in catalyst stability:
  • High surface area for both availability of active sites and adsorption of poisons.
  • High pore volume provides storage capacity for coke & metals in case of heavier feeds.
Increased resilience with more cracked feed and higher severity

- This FCCPT unit processed higher rate & more cracked stock at similar deactivation rate (DR) compared to previous cycle.
- Operating mode was changed to maximum saturation by increasing temperature resulting in significant improvement in FCC feed quality.
- The exceptional stability of the current catalyst system means the DR continues to be low even at the higher severity.

<table>
<thead>
<tr>
<th></th>
<th>ASCENT™ DN-3551</th>
<th>CENTERA™ DN-3651</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Rate, kBPD</td>
<td>BASE</td>
<td>+ 10 %</td>
</tr>
<tr>
<td>% Cracked</td>
<td>28 %</td>
<td>51 %</td>
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<tr>
<td>Feed API</td>
<td>BASE</td>
<td>- 1.9</td>
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<tr>
<td>Feed Sulfur, wt%</td>
<td>BASE</td>
<td>+ 22 %</td>
</tr>
<tr>
<td>Feed Nitrogen, ppm</td>
<td>BASE</td>
<td>+ 26 %</td>
</tr>
<tr>
<td>Feed T95, °F</td>
<td>BASE</td>
<td>BASE</td>
</tr>
<tr>
<td>Deactivation Rate, °F/m</td>
<td>1.2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>HDS Mode</td>
<td>Aromatic Saturation Mode</td>
</tr>
<tr>
<td>WABT, °F</td>
<td>BASE</td>
<td>+ 25 F</td>
</tr>
<tr>
<td>API Gain</td>
<td>BASE</td>
<td>BASE + 0.8</td>
</tr>
<tr>
<td>% HDS</td>
<td>BASE</td>
<td>+ 2 %</td>
</tr>
<tr>
<td>% HDN</td>
<td>BASE</td>
<td>+ 8 %</td>
</tr>
<tr>
<td>Diesel Sulfur</td>
<td>BASE</td>
<td>- 47 %</td>
</tr>
<tr>
<td>Deactivation Rate, °F/m</td>
<td>BASE</td>
<td>No change</td>
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</table>
Excellent Stability with Increased Operating Severity

- Operating mode for this FCCPT unit was switched to maximum aromatic saturation to target higher volume swell & H₂ consumption
- Delta API was one number higher in Asat mode
- Deactivation rate was unchanged in spite of the higher severity
Stable performance with Heavier Feed in ULSD service

- New generation catalyst maintained a 15 – 20 °F activity benefit throughout the cycle
- Refinery was able to increase straight run diesel and LCGO end point
- Average feed was heavier with higher S and N; unit achieved higher margin while maintaining cycle life

<table>
<thead>
<tr>
<th></th>
<th>CENTINEL™ DN-3330</th>
<th>CENTERA™ DN-3630</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Rate, kBPD</td>
<td>BASE</td>
<td>+ 3%</td>
</tr>
<tr>
<td>Feed S, wt%</td>
<td>BASE</td>
<td>+ 175%</td>
</tr>
<tr>
<td>Feed N, ppm</td>
<td>BASE</td>
<td>+ 22%</td>
</tr>
<tr>
<td>Feed T90 / FBP, °F</td>
<td>BASE / BASE</td>
<td>+ 22 / + 27 °F</td>
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</tbody>
</table>
Improved HCR PT Activity & Stability with Heavier HCGO

- Pretreat reactor changed to a newer generation hydrotreating and ASA catalyst system
- The current system is 8 – 10 °F higher in HDN activity with a 40% lower deactivation rate even though the HCGO end point is 20 – 40 °F higher than last cycle
- Current exotherm is 20% higher indicating increased hydrogenation
Excellent Stability leads to higher Diesel Yields

- Another FCCPT unit that processes 100% cracked feed enjoyed large increase in diesel yield with a new generation catalyst load.
- Unit was able to process more difficult feed (higher N, lower API) while maintaining yield throughout the cycle.
- Diesel T95 was 10 °F higher along with higher consumption and thus increased volume swell.

<table>
<thead>
<tr>
<th></th>
<th>ASCENT™ DN-3551 / CENTERA™ DC-2650</th>
<th>CENTERA™ DN-3651 / DC-2650</th>
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<tbody>
<tr>
<td>Feed Rate</td>
<td>BASE</td>
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<tr>
<td>LCO Rate</td>
<td>BASE</td>
<td>+ 37 %</td>
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<tr>
<td>Feed API</td>
<td>BASE</td>
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<tr>
<td>Feed Sulfur</td>
<td>BASE</td>
<td>BASE</td>
</tr>
<tr>
<td>Feed Nitrogen</td>
<td>BASE</td>
<td>+ 9 %</td>
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<tr>
<td>H₂ Consumption</td>
<td>BASE</td>
<td>+ 11 %</td>
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<tr>
<td>Diesel Yield, % of FF</td>
<td>47 %</td>
<td>52 %</td>
</tr>
<tr>
<td>Diesel T95</td>
<td>BASE</td>
<td>+ 10 °F</td>
</tr>
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</table>
Resolve dP growth with optimized grading

- This unit suffered from chronic delta P growth
- Top two beds were skimmed halfway through the cycle due to high dP
- Delta P increase has been greatly reduced since the skim as a result of grading scheme optimization (smaller catalyst in filter tray, increased grading volume and layering)
- Unit is on track to achieve 60 months cycle life compared to original target of 36 months
Summary

• In addition to catalyst activity, stability is a key performance indicator to ensure units meet turnaround timing and minimize unplanned downtime.

• New catalysts enable refiners to process higher value and more difficult feed streams without sacrificing cycle life.

• Units constrained by metals poisoning or delta P growth can be improved by a robust demet system or an optimized grading scheme and hardware options such as Shell Global Solutions HDTrays™ & Filter Trays™.

• These products combined with Criterion’s technical expertise help refiners maximize value from their assets.