Latest Developments in Middle Distillates Hydroprocessing
Agenda

- Challenge about producing ULSD
- Axens Prime-D™ Offer
- Impulse™ Technology
- Case study
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Trend for the Near Future

More stringent Specifications

- Higher ULSD demand forecasts

Need for:
- High activity Catalysts
- Revamping & Grassroots Solutions
But…

- How to handle more and more refractory feedstocks?
- What about Condensates?
ULSD Production Challenges: Cracked Feedstock

Cracked feed stocks origins:

- Thermal cracking: LCGO, VBGO
- Cracked diesel: H-Oil, MHC, ARDS/VRDS
- FCC: LCO

Cracked feedstock is refractory:

Higher level of difficult sulfur, nitrogen and polyaromatics compounds

Performance & Operation Issues:

- Poisons
- Hydrogen consumption
- Fouling
- Overtreating / feed fluctuations
- Cycle length
- Temperature effect
- Deactivation
- Little blending options

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  - LCO / LCGO
  - H-Oil Diesel
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**Refractory Feedstocks**  
**LCO & LCGO Hydroprocessing Challenges**

<table>
<thead>
<tr>
<th></th>
<th>SR Diesel</th>
<th>LCO</th>
<th>Total Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S, wt %</strong></td>
<td>0.5 – 2.0</td>
<td>0.2 - 2.5</td>
<td>0.5 – 3.0</td>
</tr>
<tr>
<td><strong>S as DBTs, wt %</strong></td>
<td>15 – 30</td>
<td>30 – 70</td>
<td>15 - 30</td>
</tr>
<tr>
<td><strong>N, wtppm</strong></td>
<td>50 - 300</td>
<td>200 - 1200</td>
<td>100 – 2000</td>
</tr>
<tr>
<td><strong>Total Aro, wt %</strong></td>
<td>20 – 30</td>
<td>65 – 90</td>
<td>30 – 50</td>
</tr>
<tr>
<td><strong>Di-Aro+, wt %</strong></td>
<td>5 – 15</td>
<td>40 – 70</td>
<td>10 – 20</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>0.830 – 0.870</td>
<td>0.900 – 0.980</td>
<td>0.850 – 0.900</td>
</tr>
<tr>
<td><strong>Cetane Number</strong></td>
<td>45 - 60</td>
<td>15 - 30</td>
<td>35 - 50</td>
</tr>
</tbody>
</table>

- Higher density / Lower cetane due to Higher aromatics content: Hydrogenation required
- Same range of total Sulfur but lots of refractory species
Refractory Feedstocks
Comprehensive Reaction Progress by GC 2D

LCO initially

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur, ppm</td>
<td>15600</td>
</tr>
<tr>
<td>Nitrogen, ppm</td>
<td>1088</td>
</tr>
<tr>
<td>Density</td>
<td>0.9415</td>
</tr>
<tr>
<td>Cetane</td>
<td>27</td>
</tr>
</tbody>
</table>
Refractory Feedstocks
Comprehensive Reaction Progress by GC 2D

LCO initially

Intermediate HDT

Tri-aros and Di-aros hydrogenated

<table>
<thead>
<tr>
<th></th>
<th>LCO initially</th>
<th>Intermediate HDT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur, ppm</td>
<td>15600</td>
<td>3</td>
</tr>
<tr>
<td>Nitrogen, ppm</td>
<td>1088</td>
<td>1.5</td>
</tr>
<tr>
<td>Density</td>
<td>0.9415</td>
<td>0.87310</td>
</tr>
<tr>
<td>Cetane</td>
<td>27</td>
<td>44</td>
</tr>
</tbody>
</table>

Aromatic Hydrogenation Equilibrium Thermodynamic Limitations

HDA Target

LHSV = 0.6 x Base
LHSV = Base
LHSV = 1.2 x Base

Thermo Limitation at 1.4 x Ref ppH2

Axens' Iran Seminar - Refining Day - 28 Tir 1396 (19 July 2017)
- Objectives:
  - Euro V specifications in diesel pool
  - 4 years life cycle

ULSD and Density & Cetane improvement targets for a mix of SRGO and LCO

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp Gr@15°C</td>
<td>0.890</td>
</tr>
<tr>
<td>Cetane Index</td>
<td>36.7</td>
</tr>
<tr>
<td>Sulfur %wt</td>
<td>1.7</td>
</tr>
</tbody>
</table>

- Medium pressure: 80 bar ppH2
- Impulse NiMo catalyst

\[ \Delta \text{Density required: } -45 \]
\[ \Delta \text{Cetane required: } 12 \]
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# Refractory Feedstocks
Diesel Effluent from Residue Upgrading

<table>
<thead>
<tr>
<th></th>
<th>SR Diesel</th>
<th>H-Oil Diesel</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>S, wt %</td>
<td>0.5 – 2.0</td>
<td>0.1- 0.5</td>
<td></td>
</tr>
<tr>
<td>N, wt ppm</td>
<td>50- 200</td>
<td>1000- 2000</td>
<td>Strong inhibition</td>
</tr>
<tr>
<td>Total Aro, wt %</td>
<td>20- 30</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>0.830 – 0.870</td>
<td>0.850- 0.870</td>
<td>Low content but refractory species</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>45- 60</td>
<td>42 - 44</td>
<td>Refractory aromatics remained after Residue conversion unit, difficult to hydrogenate</td>
</tr>
</tbody>
</table>

- **Axens’ Iran Seminar - Refining Day - 28 Tir 1396 (19 July 2017)**
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- Challenge about producing ULSD

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  - Hydrotreating Licensing
  - Catalyst Portfolio

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Design Features
Prime-D™ Process Optimization

Robust, Highly reliable and Energy efficient Prime-D™ process

- EquiFlow®
- Hy-Tray™ & Hy-Quench™
- Improved distribution
- Improved Mixing efficiency
- Highly compact mixing boxes
- Higher flexibility

- Custom & Efficient Early Design
  - In House software for Heat Exchangers network optimisation
  - Strong knowledge in Energy Efficiency

High efficiency Heat Exchangers
- Spiral Tube exchanger (ZPJE) or Welded Plate exchanger (Packinox)
- Compacity
- CAPEX & OPEX reduction
Reactor Internals: EquiFlow® Hy-Tray™ and Hy-Quench™

- **New Quench Box developed**
  - Flexibility of operation
  - Improved Mixing Efficiency
  - Height Reduction – Compact Design

Example for HCK service: new design showed potential for 10% more catalyst for a given typical reactor with several beds

**Significant Gain**

**Space reduction: up to 800 mm**
CEED: Collaborative Phase & Powerful Decision-Support Tool

A lot of exchanges with customer in a tight schedule...

- Number of weeks before H&MB / PFD finalization
  - Base
  - Base + 3 weeks
  - Base + 100% (x 2)

... To propose various options evaluated using several criteria selected by the customer ⇒ A powerful decision-support tool

100 Basis Index for Base Case (Option A)

- CAPEX
- ENERGY Utilities Consumption
- WATER Consumption
- CO₂ Emissions
- NPV (Net Present Value) @10%, 15 years

After licensor selection

Options
- A: Base Case
- B: Low Energy
- C: Very Low Energy
- D: Low Water

+ Dedicated operability report for each option

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Axens’ Unique Position Catalyst Portfolio

Challenges

- Conventional HDS/HDT Target
  - With low H₂ consumption
- Cracked/Heavy Feedstock
- Maximum Aromatics Saturation
  - Volume Swell / Density Reduction
  - High Cetane Gain
- Max T95/Density Reduction
- CFP Improvement
- Vegetal Oil Co Processing

Solutions

✓ Highly active, outstandingly stable HDT catalysts
  - CoMo / NiMo Catalysts
  - Ace™ & Impulse™ series
  - Combined with Stacking knowledge

✓ Grading Strategy
  - Scale Traps
  - Iron Sulfide, Si, Ni+V, As traps
  - Di-olefins and Olefin saturation catalyst

✓ Complete Catalyst Portfolio
  - Dewaxing / Cracking / Noble Metals solutions
# Middle Distillates Hydroprocessing Catalysts

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>CoMo</th>
<th>NiMo</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unit Pressure</strong></td>
<td>Low to Medium</td>
<td>Medium To High</td>
</tr>
<tr>
<td><strong>Target</strong></td>
<td>High HDS</td>
<td>Max HDS</td>
</tr>
<tr>
<td><strong>Products</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HR 616</td>
<td>HR 1246</td>
<td>HR 608</td>
</tr>
<tr>
<td>HR 626</td>
<td></td>
<td>HR 648</td>
</tr>
<tr>
<td><strong>Achievements</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HDS services</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower ( \text{H}_2 ) cons.</td>
<td>Highest HDS Activity</td>
<td>Highest HDS &amp; HDA Activity</td>
</tr>
<tr>
<td>HDT services</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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Refractory Feedstocks

- Heavy Coker Gasoil – HCGO
- Heavy Light Cycle Oil – LCO
- Bitumen derived Diesel (Venezuelian crudes, ...)

Refractory feedstocks = Low cost = High profit!

Upgrade required to:

✓ Produce low Sulfur Diesel
✓ Maximize volume swell
✓ Product Properties Improvement (Cetane; Distillation)

- H-Oil® Diesel (ebullated bed)
- Coal Tar Diesel
- Vegetable fat Oil
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General Conclusion

Process Licensor + Catalyst Manufacturer Combination = maximum client satisfaction

Extensive Licensing Experience

New Superior Performance Impulse™ Catalysts

Unrivaled Refining Profitability
Thank you! And see you on Axens’ Blog
axens.net/blog