Advances in Hydroprocessing Catalysts

International Conference on
‘Refining Challenges- Way forward’
April 16-17, 2012
Organised by Petrofed, New Delhi, India

Laxmi Narasimhan
General Manager
Centre for Novel Catalytic Materials
Shell Technology Centre
Shell India Marketing pvt Limited, Bangalore
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Agenda

- About Shell Technology Centre, Bangalore
- New Directions in Hydroprocessing R&D
  - Hydrocracking
  - Beyond ULSD
    - Case study
  - Heavy Oil upgradation
Three Business Units

CRI/Criterion Inc. Family

Upstream & Renewables
- GTL
- Acid & Heavy Crude
- \( \text{H}_2 / \text{Membranes} \)
- Renewable Fuels & Chemicals

Refining
- Naptha HT
- Distillate HT
- Hydrocracking
- FCC Pretreat
- Lubes
- Resid Upgrading
- Tail Gas
- Clean Fuel Projects

Chemicals
- Ethylene Oxide
- Selective Hydrogenation
- Environmental
Enhancing R&D effectiveness by deploying High throughput tools

Parallel catalyst preparation unit

Parallel pelletizing, crushing and sieving tools

16 barrel unit for hydroprocessing

16 barrel unit for flue gas applications

Conditions:
1. $T_{\text{max}} = 500 \, ^\circ\text{C}$
2. Pressure = 1-100 bar
3. Online GC
4. S/N analyzer

Conditions:
1. $T_{\text{max}} = 800 \, ^\circ\text{C}$
2. Pressure = 1-12 bar
3. MS analyzer
THE FOUR Cs APPROACH
Customizing catalysts for hydrotreating

Chemistry (HDN/HDS)

Composition (feed blend)

Conditions (Unit operation & limitations)

Catalyst (Activity, stability, shape & selectivity)
**State-of-the Art Technology  HCU Catalysts**

**D-VUSY compared to VUSY**

- More active Y zeolites
- Same intrinsic VUSY type selectivity

**Gives**

- Higher binder content
- Extra room for hydrogenating metals
- Room to add extra functionality

**How utilized**

- Zeolites with content & activity/selectivity optimized to catalysts type
- Morphology to maximize access of feed molecules
- Metals balanced to binder surface for premium products
- Third function to enhance other chemistries
  - Aromatics saturation
  - Cold Flow property improvement
- Selectivity enhancements
Zeolyst Hydrocracking Portfolio

Similar Surface Area
200 – 230m²/g
Moving zeolite manufacturing into the 21st century

Direct feedback from R&D to manufacturing.

“Nano-scale” engineered materials are feasible at industrial-scale productions.

“Nano-scale” engineered materials produced at industrial scale.
Beyond ULSD: Motivation (1)

- Refinery Business Drivers -- Evolution:
  - Increased Heavy/Sour Crude Processing
  - Increased Bottoms Conversion
  - Increased Distillates Production/Product Quality (Higher Cetane, Lower Aromatics Content, etc.)

- ULSD Unit Flexibility: Capture Changing Opportunities
Significant S & Dramatic N Increases with Increasing Incremental Boiling Range.
Feed Effects: Hydrotreating Catalyst Inhibition

Moderate Pressure Hydrotreater Conditions & NiMo/Al$_2$O$_3$ Catalyst

![Graph showing the effect of relative inhibitor molar concentration on initial 4,6-DM-DBT HDS rate.](image)

Organic N: Strongest Inhibitor
Increasing Feed N Increases Catalyst Inhibition.

Beyond ULSD: Motivation (3)

- Solutions: Rapid Implementation / Immediate Economic Payback
- Commercially Proven – Low Risk
- Multiple Technologies Available
  - Optimal Solution – Refinery/Unit Specific

Drivers:
- “Clean” Product
- Hydrogenation Environment
Catalyst Technology
High Performance Catalysts: Enhance Feed/Product Quality Flexibility

- High Performance Catalysts:
  - Reduce HT Catalyst Requirements
  - Make Reactor Volume Available – Speciality Catalysts
  - Enable Additional Upgrading Reactions Possible

Current or Design
ULSD

Gen 1 ULSD

Gen 1 ULSD

Gen 1 ULSD

Current or Design
ULSD

Future
Enhanced Diesel
Operation

Gen 1 ULSD

GEN 1 ULSD

GEN 1 ULSD

Future Enhanced Diesel Operation

CENTERA
Or Other

CENTERA
Or Other

CENTERA
Or Other

CENTERA
Or Other

CENTERA
Or Other

Aromatic
Saturation

Selective
Ring Opening

Cracking

Isomerization

Upgrading
Chemistry

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Selective Hydrocracking in ULSD Operations: (SRO and MHC)

- **Technology Drivers**
  - Fills ULSD/Hydrocracking Performance Gap
  - Cheaper H₂: Improves Economic Viability
  - Operating Flexibility: Maximize Product Margin
Introduction/Background

• Pilot Plant Study – Grass Roots ULSD Unit Project
  ■ ULSD Test
  ■ ULSD/MHC Test

• Unit Design Objectives
  ■ Gasoline/Distillate Flexibility
  ■ Cetane Improvement
## ULSD/MHC Operation: Gasoline/Distillate Flexibility

### Feed Blend, Process Conditions, & Catalyst Systems Tested

<table>
<thead>
<tr>
<th>Feed Blend (Vol%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SRD</td>
<td>55</td>
</tr>
<tr>
<td>LCGO</td>
<td>23</td>
</tr>
<tr>
<td>LCO</td>
<td>11</td>
</tr>
<tr>
<td>CN</td>
<td>11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ULSD Process Conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LHSV (hr⁻¹)</td>
<td>1.0</td>
</tr>
<tr>
<td>ppH₂ (psia)</td>
<td>75</td>
</tr>
<tr>
<td>H₂/Oil (SCFB)</td>
<td>420</td>
</tr>
<tr>
<td>WABT (°F)</td>
<td>340</td>
</tr>
<tr>
<td>Catalyst</td>
<td>DN-3110</td>
</tr>
</tbody>
</table>

### ULSD/MHC Process Conditions

<table>
<thead>
<tr>
<th>ULSD/MHC Process Conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LHSV (hr⁻¹)</td>
<td>0.9</td>
</tr>
<tr>
<td>ppH₂ (psia)</td>
<td>75</td>
</tr>
<tr>
<td>H₂/Oil (SCFB)</td>
<td>710</td>
</tr>
<tr>
<td>WABT (°F)</td>
<td>340 - 350</td>
</tr>
<tr>
<td>Catalyst</td>
<td>NiMo/HC (85/15 –Vol/Vol)</td>
</tr>
</tbody>
</table>

- **Substantial Cracked Stocks**
- **Catalyst Volumes Adjusted to Provide Equal HDS Activity**
### ULSD/MHC Operation: G/D Flexibility - ULSD Operation

**ULSD Operation Product Quality: Significant Cetane Upgrade with Minimal Distillate Yield Loss**

<table>
<thead>
<tr>
<th>ULSD</th>
<th>Feed</th>
<th>TLP</th>
<th>Diesel</th>
<th>Naphtha</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>193°C+</td>
<td>193°C-</td>
<td></td>
</tr>
<tr>
<td>Density @ 15 C (g/cc)</td>
<td>0.8664</td>
<td>0.8423</td>
<td>0.8536</td>
<td>0.7720</td>
</tr>
<tr>
<td>Sulfur (wppm)</td>
<td>7800</td>
<td>7</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Nitrogen (wppm)</td>
<td>275</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>SFC Aromatics (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mono-</td>
<td>30.0</td>
<td>-----</td>
<td>21.2</td>
<td>15.9</td>
</tr>
<tr>
<td>Di-</td>
<td>10.6</td>
<td>-----</td>
<td>2.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Tri-</td>
<td>1.1</td>
<td>-----</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Tetra+</td>
<td>0.7</td>
<td>-----</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>42.4</strong></td>
<td>-----</td>
<td><strong>24.2</strong></td>
<td><strong>16.1</strong></td>
</tr>
<tr>
<td>Hydrogen Consumption (Nl/l)</td>
<td></td>
<td>116</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cetane Index (D-4737-A)</td>
<td>36.8</td>
<td><strong>43.8</strong></td>
<td><strong>45.1</strong></td>
<td>-----</td>
</tr>
<tr>
<td>D-86 Distillation, (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP</td>
<td>62</td>
<td>121</td>
<td>212</td>
<td>92</td>
</tr>
<tr>
<td>5 vol%</td>
<td>127</td>
<td>158</td>
<td>227</td>
<td>110</td>
</tr>
<tr>
<td>50%</td>
<td>262</td>
<td>251</td>
<td>260</td>
<td>146</td>
</tr>
<tr>
<td>95%</td>
<td>324</td>
<td>319</td>
<td>329</td>
<td>183</td>
</tr>
<tr>
<td>FBP</td>
<td>332</td>
<td>329</td>
<td>332</td>
<td>191</td>
</tr>
<tr>
<td>Incremental 82-193°C (vol%)</td>
<td>0</td>
<td>1.1</td>
<td>-----</td>
<td></td>
</tr>
</tbody>
</table>

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ULSD/MHC Operation: Gasoline/Distillate Flexibility

ULSD/MHC Product Quality: Extensive Cetane Upgrade

ULSD/MHC Yields: Significant Naphtha Production & T-95 Shift

<table>
<thead>
<tr>
<th>ULSD/MHC</th>
<th>WABT = 340°C</th>
<th></th>
<th>WABT = 350°C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>TLP</td>
<td>Diesel</td>
<td>Naphtha</td>
</tr>
<tr>
<td>Density @ 15 C (g/cc)</td>
<td>0.8664</td>
<td>0.8286</td>
<td>0.8420</td>
<td>0.7840</td>
</tr>
<tr>
<td>Sulfur (wppm)</td>
<td>7800</td>
<td>2</td>
<td>3</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Nitrogen (wppm)</td>
<td>275</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>SFC Aromatics (wt%)</td>
<td>30.0</td>
<td>-----</td>
<td>10.9</td>
<td>16.7</td>
</tr>
<tr>
<td>Mono-</td>
<td>10.6</td>
<td>-----</td>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Di-</td>
<td>1.1</td>
<td>-----</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Tri-</td>
<td>0.7</td>
<td>-----</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Total</td>
<td>42.4</td>
<td>-----</td>
<td>11.8</td>
<td>16.8</td>
</tr>
<tr>
<td>Hydrogen Consumption (Nl/l)</td>
<td>150</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cetane Index (D-4737-A)</td>
<td><strong>36.8</strong></td>
<td><strong>46.2</strong></td>
<td>49.1</td>
<td>-----</td>
</tr>
<tr>
<td>D-86 Distillation (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP</td>
<td>62</td>
<td>109</td>
<td>203</td>
<td>92</td>
</tr>
<tr>
<td>5 vol%</td>
<td>127</td>
<td>142</td>
<td>231</td>
<td>113</td>
</tr>
<tr>
<td>50%</td>
<td>262</td>
<td>243</td>
<td>257</td>
<td>149</td>
</tr>
<tr>
<td>95%</td>
<td><strong>324</strong></td>
<td><strong>312</strong></td>
<td>324</td>
<td>188</td>
</tr>
<tr>
<td>FBP</td>
<td>332</td>
<td>321</td>
<td>326</td>
<td>193</td>
</tr>
<tr>
<td>Incremental 82-193°C (vol%)</td>
<td>0</td>
<td><strong>9.6</strong></td>
<td>-----</td>
<td></td>
</tr>
</tbody>
</table>
Enhanced Aromatic Saturation (EAS)

- Extension of Aromatic Saturation Technology
  - (Base Metal) Catalyst
    - Higher Aromatic Saturation (ASAT) Levels
  - Process
    - Uniform Product Quality: SOR/EOR
    - Liquid Quench – Temperature Management / Compressor Design
Enhanced Aromatic Saturation (EAS) Case Study

- **Issue**
  - Increase ULSD Product Volumes
  - Maximize LCO → Diesel Pool (SOR/EOR - Throughout Cycle)
  - CI Loss SOR → EOR: 1-2 CI Numbers
    - Throughput Reduction: 1-2 kB/D

- **Solution**
  - Revamp Moderate Pressure DHT
    - Base Metal Catalyst
    - Minor Process Modifications
    - Treat Maximum LCO

- **Value to Customer**
  - €3M/YR
    (Increased Diesel Yield)

---

ULSD/EAS Operations at MOR Conditions*

<table>
<thead>
<tr>
<th>Property</th>
<th>Feed Origin</th>
<th>Product LCO/Hydrotreated - 55/45 (Vol Basis)</th>
<th>Delta or Conv (Feed-Prod or %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane Index</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM D-4737-A</td>
<td>28.0</td>
<td>37.9</td>
<td>9.9</td>
</tr>
<tr>
<td>UV Aromatics (wt%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PNA</td>
<td>24.31</td>
<td>0.92</td>
<td>96%</td>
</tr>
<tr>
<td>Total</td>
<td>36.16</td>
<td>15.37</td>
<td>57%</td>
</tr>
<tr>
<td>Distillation D-2887 (°C) wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>209</td>
<td>196</td>
<td>13</td>
</tr>
<tr>
<td>50</td>
<td>275</td>
<td>257</td>
<td>18</td>
</tr>
<tr>
<td>90</td>
<td>344</td>
<td>330</td>
<td>14</td>
</tr>
<tr>
<td>95</td>
<td>358</td>
<td>351</td>
<td>8</td>
</tr>
</tbody>
</table>

* Max Reactor Temperatures ~ 375 °C
Diesel Catalytic Dewaxing (DCDW)

⇒ Economic Drivers – Cold Flow Improvement / Diesel Yield Preservation

- **ENABLER:** shape-selective zeolites
  - Meet seasonal cold flow properties
  - Reduce additives
  - Increase diesel endpoint / volume
  - Minimise kero blending
    (jet value high in places)

![Diagram showing single and two-stage dewaxing processes with chemical reactions and product separation.](image-url)

**Single Stage Dewaxing**

- **Selective Paraffin Hydrocracking:**
  - $\text{H}_2$ Consumption & $\Delta H_{\text{RXN}}$
  - $\text{H}_2$
  - (Many Possible Cracking Products)

**Paraffin Isomerization:**

- No $\text{H}_2$ Consumption & Very Low $\Delta H_{\text{RXN}}$
- (Many Possible Isomers)

**Two-Stage Dewaxing**
Case Study: Multiple Upgrading Options

- Issue
  - Upgrade a range of low quality diesel streams (LCO, LVGO)
  - Multiple upgrading objectives and two different operating modes
  - Do all upgrading in a single unit

### Feed Information

<table>
<thead>
<tr>
<th>Feed Blend, wt%</th>
<th>ULSD Mode</th>
<th>Upgrading Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCO</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>SRGO1</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>SRGO2</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>875.3</td>
<td>862.0</td>
</tr>
<tr>
<td>Sulphur, wppm</td>
<td>1813</td>
<td>1412</td>
</tr>
<tr>
<td>Total nitrogen, wppm</td>
<td>1181</td>
<td>682</td>
</tr>
<tr>
<td>Solidification point, °C</td>
<td>0.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Cetane number</td>
<td>30.5</td>
<td>35.6</td>
</tr>
</tbody>
</table>

ULSD Mode Upgraded Mode
Case Study 2 – Multiple Upgrading Options

- **Solution**
  - Combine dewaxing catalyst for seasonal cold flow improvement of LVGO components with a mild hydrocracking catalyst to upgrade LCO to meet both jet smoke point and diesel cetane specifications

- **Value to Customer**
  - Single unit design
  - Minimise capital investment
    (P ~ 90 barg, LHSV = 1.5 hr⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>Hydrotreating Mode</th>
<th>Upgrading Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Yields, wt%</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td>1.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Naphtha</td>
<td>1.4</td>
<td>4.0</td>
</tr>
<tr>
<td>Jet Fuel</td>
<td></td>
<td>23.2</td>
</tr>
<tr>
<td>Diesel</td>
<td>98.3</td>
<td>72.0</td>
</tr>
<tr>
<td><strong>Kero Properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>816.3</td>
<td>816.8</td>
</tr>
<tr>
<td>Smoke Point, mm</td>
<td>12.4</td>
<td>21.3</td>
</tr>
<tr>
<td><strong>Diesel Properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>844.4</td>
<td>832.1</td>
</tr>
<tr>
<td>Sulphur, wppm</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Solidification point, °C</td>
<td>0</td>
<td>-9</td>
</tr>
<tr>
<td>Cetane number</td>
<td>35.6</td>
<td>47.8</td>
</tr>
</tbody>
</table>
Heavy Oil conversion

Catalyst surface processing Diesel

Same catalyst surface processing Atm. Resid
Overview of the Shell Pernis Hycon unit reactor section

Vacuum Residue feed
Hydrogen

Fresh cat. Fresh cat. Fresh cat.


HDM section HCON section

Products to work-up section
EOR Catalyst Stability performance advantage of customised catalyst (Catalyst C) measured through use of catboxes in Fixed Bed Section

Catalyst B not suitable for a 22 month cycle

- Fresh Cat B
- Fresh Cat C
- Spent Cat B ex cat box Hycon
- Spent Cat C ex cat box Hycon

Required temperature for HDS vs Hours on Stream
Conclusions

- Hydroprocessing Catalysts play key role in future of Refining Industry
- Major directions
  - Selective Hydrocracking pushing limits of selectivity (better pre-treat and specially engineered Zeolite combinations)
  - Low Hydrogen consumption
  - Beyond ULSD – HT/MHC combination for jet & diesel
  - Enhanced Aromatic saturation
  - LCO upgradation
  - Heavy Oil upgradation