Technology for Producing Clean Diesel Utilizing Moderate Pressure Hydrocracking With Hydroisomerization

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Outline

• Overview of selected ExxonMobil technologies
  • MPHC for plus production of diesel
  • Use of post treat units to adjust diesel properties through HDT, HDC and Hydroisomerization (MIDW™)
• Combining MIDW with MPHC for incremental high quality diesel
• Case study
EMRE Technologies for Quality Fuels

EMRE HYDROFINDING

Naphtha
- FCC Naphtha
- SCANfining™
- OCTGAI NSM
- Hydrofining

Distillate
- ULSD
- ULSD + MAXSAT™
- ULSD + HDHDC

Waxy Feeds
- MDDW™
- MI DW™

Heavy Feeds
- MPHC
- GO-finining™
- Residfining
- LCO Upgrading
- MPHC + MI DW

ULSD + HDHDC

KBR
Energy and Chemicals
Processing Options for Clean Distillate Fuels

- Ultra Low Sulfur HDS
- Dewaxing
- Dearomatization
- Processing LCO and other Tough Feeds
- MPHC for Plus Production

Optimum Depends Upon Desired Diesel Quantity and Quality
## MPHC - Typical Operations

### Range of Conditions

<table>
<thead>
<tr>
<th></th>
<th>Conversion</th>
<th>Pressure</th>
<th>LHSV</th>
<th>Recycle Gas</th>
<th>WABT</th>
<th>Operating Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>%wt.</td>
<td>20 – 70</td>
<td>70 – 140</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>barg</td>
<td>0.3 – 1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v/v-hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nm³/m³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>months</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

### Utilities per 1000 BPSD *

<table>
<thead>
<tr>
<th></th>
<th>kW</th>
<th>kW</th>
<th>kg/hr</th>
<th>m³/hr</th>
<th>m³/hr</th>
<th>m³/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric Power</td>
<td>240</td>
<td>835</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel (abs duty)</td>
<td></td>
<td></td>
<td>(350)</td>
<td>0.5</td>
<td>22</td>
<td>5.</td>
</tr>
<tr>
<td>MP Steam</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BFW</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooling Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lean Amine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wash Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

*Note: Middle East VGO Feed*
## Typical MPHC Performance

<table>
<thead>
<tr>
<th></th>
<th>%wt.</th>
<th>30</th>
<th>50</th>
<th>50</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion H₂ Pressure</td>
<td>%wt.</td>
<td>30</td>
<td>50</td>
<td>50</td>
<td>70</td>
</tr>
<tr>
<td>H₂ Consumption</td>
<td>Nm3/m3</td>
<td>90</td>
<td>115</td>
<td>160</td>
<td>219</td>
</tr>
<tr>
<td>Kerosene Properties</td>
<td>wppm</td>
<td>30</td>
<td>10</td>
<td>5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>mm</td>
<td>13</td>
<td>14</td>
<td>17</td>
<td>22</td>
</tr>
<tr>
<td>Smoke Pt.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diesel Properties</td>
<td>wppm</td>
<td>50</td>
<td>30</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>%w</td>
<td>43</td>
<td>45</td>
<td>50</td>
<td>55</td>
</tr>
<tr>
<td>Cetane No.</td>
<td>%w</td>
<td>50</td>
<td>55</td>
<td>35</td>
<td>25</td>
</tr>
<tr>
<td>Aromatics</td>
<td>%w</td>
<td>18</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Poly-Aromatics</td>
<td>%w</td>
<td>18</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

Note: Middle East VGO Feedstock
MPHC Process Flow Diagram

- Typical hydroprocessing flow sheet
- Reactor design and internals important
- Post treating unit or MIDW reactor to improve quality / conversion
## High vs. Moderate Pressure

<table>
<thead>
<tr>
<th>Unit</th>
<th>MPHHC</th>
<th>HPHC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion, %</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Pressure, barg</td>
<td>100</td>
<td>165</td>
</tr>
<tr>
<td>Installed Cost, US$</td>
<td>Base</td>
<td>Base + 20</td>
</tr>
<tr>
<td>Diesel Properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>&lt;50</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Cetane Index</td>
<td>45 - 55</td>
<td>55 - 65</td>
</tr>
<tr>
<td>p- Aromatics</td>
<td>5 - 10</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Hydrogen Demand</td>
<td>Base</td>
<td>Base x 1.4</td>
</tr>
</tbody>
</table>
MPHC with Integrated Diesel Treating Design (1)

(1) Danzinger at al. ERTC 2006
MPHC With PTU Integrated

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Research & Engineering

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Diesel Composition Strongly Effects Cetane

- Long branched single rings best for cetane
- N-Paraffins have good cetane but poor cold flow properties
- LCO composition limits cetane improvement
  + Aromatics saturation provides some improvement low 40’s
  + Hydrocracking and ring opening required

MPHC and MIDW Excellent Technology Choices
Cetane and Gravity Improvement vs. Aromatic Saturation

Cetane No. Increase vs. Aromatics Removed, wt%

API Gravity Increase vs. Aromatics Removed, wt%
Diesel Cetane Improvement - Hydrocracking
Feed Cetane Index = 52

Pressure = 600 psig

Pressure = 1000 psig

Temperature, F

Cetane Index

66 65 64 63 62

Feed Cetane Index = 52

HDT only
HDHDC

HDT only

HDHDC
MIDW - A Novel Dewaxing Process

- **Mobil Isomerization Dewaxing**
- Isomerizes waxy n-paraffins in gas oils
- Proprietary ExxonMobil family of catalysts
- Low pressure fixed-bed process
- Commercially proven
ExxonMobil Diesel Dewaxing Technology

- Diesel selectivity controlled by zeolite type, formulation and conditions

![Graph showing Cloud Point Reduction vs. 300°F Yield (150°C+)].

MDDW (ZSM-5) Operating “Line”

MIDW Operating “Range”
Technology for Producing Winter Diesel

- Reduce sulfur and convert paraffins to improve cold flow properties
- Maintain or improve cetane with high yields of quality diesel fuel

**Process Conditions**
- 1 or 2 stage reactors
- Conv. or MIDW catalysts
- Long cycle lengths
- Low H₂ consumption

**Diesel Product**
- < 10 wppm S
- Cetane improv. +5
- Cloud point: −50 °C

**Feeds**
- Virgin & cracked
- 0.2 to 2.0 % S
- 30 – 50 CI

ExxonMobil’s MIDW is Leading Technology for Winter Diesel
MIDW Reactor Configurations

Waxy Feed → MIDW → Low Pour, High Cetane Diesel

Moderate S, N → HDT → MIDW → Lower Reactor Temperatures
Low Sulfur Distillates

High S, N → HDT → MIDW → Lower Reactor Temperatures
Higher Distillate Yields

VGO Feed → MPHC → MIDW → Premium Quality Distillates
Low Pour Point Bottoms
Long Catalyst Life
MPHC/MIDW Integration for High Conversion

- MPHC (Stage 1)
  - Stage 1 bottoms
  - HYDROGEN
- MIDW (Stage 2)
  - FEED
  - Integrated Product Recovery Section
  - DISTILLATES
- JET FUEL
- PREMIUM DIESEL
- VLS FCC FEED

FEED:
- HAGO
- VGO
- HVGO
- LCO
- HCGO
- LCGO
- DAO

MIDW (Stage 2):
- MPHC (Stage 1) bottoms
- HYDROGEN

MPHC/MIDW Integration for High Conversion

EXxonMobil
Research & Engineering

KBR
Energy and Chemicals
## MIDW Product Inspections

<table>
<thead>
<tr>
<th></th>
<th>Feedstock</th>
<th>Naphtha</th>
<th>Kerosene</th>
<th>Diesel</th>
<th>LSHFO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Boiling Range, °C</strong></td>
<td>350-510</td>
<td>C5-150</td>
<td>150-255</td>
<td>255-388</td>
<td>388+</td>
</tr>
<tr>
<td><strong>Yield, Vol%</strong></td>
<td>100.0</td>
<td>22.9</td>
<td>21.5</td>
<td>19.2</td>
<td>36.8</td>
</tr>
<tr>
<td><strong>Gravity, ° API</strong></td>
<td>32.0</td>
<td>73.0</td>
<td>49.5</td>
<td>34.7</td>
<td>29.5</td>
</tr>
<tr>
<td><strong>Sulfur, ppm wt</strong></td>
<td>260</td>
<td>&lt;1</td>
<td>2</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td><strong>Smoke, mm</strong></td>
<td>-</td>
<td>-</td>
<td>32</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Freeze, ° C</strong></td>
<td>-</td>
<td>-</td>
<td>&lt;-54</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Pour Point, ° C</strong></td>
<td>&gt;38</td>
<td>-</td>
<td>-</td>
<td>-43</td>
<td>&lt;-7</td>
</tr>
<tr>
<td><strong>Cetane Index</strong></td>
<td>-</td>
<td>-</td>
<td>52</td>
<td>56</td>
<td>-</td>
</tr>
<tr>
<td><strong>P/N/A, wt%</strong></td>
<td>44/39/17</td>
<td>-</td>
<td>-/-10</td>
<td>45/31/24</td>
<td>36/42/22</td>
</tr>
</tbody>
</table>
Case Study

- Goal: achieve high conversion economically
- Feed: Middle East crude HVGO
- Configuration: MPHC for stage 1 and MIDW for stage 2
- Optimize conversion in each stage
- High jet yield preferred
- Estimate yields and qualities
### MPHC/MIDW Reactor Operating Conditions

<table>
<thead>
<tr>
<th></th>
<th>MPHC</th>
<th>MIDW</th>
<th>Combined</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion, wt%</td>
<td>55%</td>
<td>55%</td>
<td>80%</td>
</tr>
<tr>
<td>Feed Rate, % of Fresh Feed</td>
<td>100</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Chemical H₂ Consumption</td>
<td>Nm³/m³</td>
<td></td>
<td>280</td>
</tr>
<tr>
<td>Reactor Inlet Pressure</td>
<td>Barg</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Minimum Cycle Length</td>
<td>Months</td>
<td>24</td>
<td>48</td>
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</table>
## Yields and Product Qualities (SOR)

<table>
<thead>
<tr>
<th></th>
<th>wt%</th>
<th>Bottoms</th>
<th>Diesel</th>
<th>Jet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield on Fresh Feed</td>
<td>wt%</td>
<td>20</td>
<td>20</td>
<td>31</td>
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<tr>
<td>SG</td>
<td></td>
<td>0.850</td>
<td>0.837</td>
<td>0.802</td>
</tr>
<tr>
<td>Sulfur</td>
<td>ppmw</td>
<td>&lt;10</td>
<td>&lt;6</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Cloud Point</td>
<td>°C</td>
<td>-18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freeze Point</td>
<td>°C</td>
<td></td>
<td></td>
<td>-50</td>
</tr>
<tr>
<td>Smoke Point</td>
<td>mm</td>
<td></td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Total Aromatics</td>
<td>wt%</td>
<td>12.2</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>PNA</td>
<td>wt%</td>
<td>1.6</td>
<td>0.1</td>
<td></td>
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<tr>
<td>Centane Index, D976-80</td>
<td></td>
<td>56</td>
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<tr>
<td>Centane Index, D4737</td>
<td></td>
<td>66</td>
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<td></td>
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<tr>
<td>Hydrogen Content</td>
<td>wt%</td>
<td>&gt;14</td>
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</table>
# Comparison of Options for High Conversion

<table>
<thead>
<tr>
<th></th>
<th>2 Stage MPHC</th>
<th>1 Stage HPHC</th>
<th>2 Stage MPHC with Recycle</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conversion</strong></td>
<td>85%</td>
<td>75-85%</td>
<td>&gt;95%</td>
</tr>
<tr>
<td><strong>Capital Investment</strong></td>
<td>Base</td>
<td>Base</td>
<td>Base +50%</td>
</tr>
<tr>
<td><strong>Hydrogen Consumption</strong></td>
<td>Base</td>
<td>Base x 1.2</td>
<td>Base x 1.3</td>
</tr>
<tr>
<td><strong>Distillate Yield</strong></td>
<td>Base</td>
<td>Base – 2%</td>
<td>Base +6%</td>
</tr>
<tr>
<td><strong>Reactor Fabrication</strong></td>
<td>Rolled Plate</td>
<td>Forged</td>
<td>Forged</td>
</tr>
<tr>
<td><strong>Reactor Delivery</strong></td>
<td>24-26 months</td>
<td>36-40 months</td>
<td>36-40 months</td>
</tr>
</tbody>
</table>
2 Stage Integrated MPHC/MIDW Advantages

- Better overall yield
  - No extra cracking to lighter products.
- Better product properties
  - MIDW catalyst in 2\textsuperscript{nd} stage - better distillate qualities and cold flow properties
  - Unit will make Euro IV diesel spec - density, CI better than HP operations
  - Jet - better smoke point and freeze point
- Flexible 2 stage design
  - Easy transition between max-diesel or max-jet operation
  - Optimize conversion between two systems
  - Option to process external feeds
- Lower pressure and no reprocessing hydraulics
  - Lower TIC
  - Lower hydrogen consumption/compression
  - Lower ops cost
  - Improved operability, reliability, and safety
  - Easier and shorter turnaround
  - Favorable project execution
  - Better reactors/compressor delivery
Conclusions

• A number of processing and catalyst options available
  + Optimum choice depends upon specific quality / quantity needed

• MPHC combined with MIDW allows high pressure performance at low operating cost

• ExxonMobil has the technology and extensive operating experience
  + Well positioned to assist customers in meeting their requirements