Processing Options for Shale Oil Upgrading

Shale Oil 32nd Symposium

Colorado School of Mines

October 15-17, 2012
INTRODUCTION TO CLG

Chevron Lummus Global (CLG) – A 50:50 Joint Venture
CLG is a 50:50 JV between Chevron and CB&I Lummus

Chevron Lummus Global
Chevron/Richmond, CA

Headquarters
Research and Development
Main Labs.
Proposals
Engineering
Marketing

Chevron Lummus Global
Bloomfield, NJ

Proposals
Engineering
Marketing
Process & R&D
Development

A Chevron and Lummus Technologies Joint Venture
Introduction to CLG

Chevron History in Hydroprocessing

- Chevron begins Hydrocracking R&D in 1959
- First Hydrocracking Licensee starts up in 1962
- Chevron Pascagoula Hydrocracker starts up in 1963
- Chevron Richmond Hydrocrackers start up in 1966 – Today, 10 high-pressure reactors!

Where We Are Today

- 7 wholly owned Chevron refineries have 73 hydroprocessing reactors (41 high-pressure and 32 < 1000 psi)
- 6 partially owned Chevron refineries (Caltex) have 40 hydroprocessing reactors
- Has the Highest Hydroprocessing to Crude Throughput Ratio in North America
- All Chevron hydroprocessing units are linked into the Chevron Hydroprocessing Best Practice Network
- Nearly 300 CLG hydroprocessing licensees world-wide!
Introduction to CLG

Pilot Plant Facilities

- 25+ Pilot Plants
- Complete Miniatures of Commercial Hydroprocessing Units
- Catalyst Charges: 100 cc to 20 Liters
- Feeds: Naphtha Through Vacuum Resid from Petroleum, Syncrude, Shale Oil, Coal, GTL, Biofuels
- Operator Coverage 24 Hours Per Day
- Pilot Plant Data Used to Design Commercial Hydroprocessing Units and Evaluate new Catalysts and Process Innovations
- Large Cold Flow Models For Reactor Internals
- Fixed Bed Downflow, Upflow, and Ebullated Bed Reactors
Micro-Unit Facilities

- 80+ Micro-Units Located in Several Labs
- Micro-Unit Features
  - Small Reactors, 2 – 10 cc Catalyst
  - Can Feed Both Pure Compounds and Petroleum Fractions (liquid and/or gas); Require Small Quantities of Feedstock
  - Quick Determination of Activity and Yield and Product Qualities
  - Quick Comparison of Different Catalyst Systems
UPGRADING SHALE OIL

Shale Oil Characteristics and Upgrading Options
Nature of Shale Oil

- Shale oil from various regions differs significantly in characteristics and is dependent on method of recovery.

- Oil shale kerogen must be heated to 650 to 750 °F for in-situ pyrolysis – the quality of shale oil is much better (lower contaminants and higher API) but recovery takes long (years) and recovered oil is less.

- Surface retorting between 900 and 1000°F recovers shale oil faster and more of it but the quality is not as good (lower API, much higher contaminants).

- Contaminants sometimes tend to distribute throughout all boiling ranges.
# Raw Shale Oil Properties

## Feed Characteristics

<table>
<thead>
<tr>
<th>Property</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>API</td>
<td>15 - 33</td>
</tr>
<tr>
<td>Sulfur, wt.%</td>
<td>0.24 – 9.32</td>
</tr>
<tr>
<td>Nitrogen, wt.%</td>
<td>0.34 – 2.16</td>
</tr>
<tr>
<td>Oxygen, wt.%</td>
<td>0.63 – 6.1</td>
</tr>
<tr>
<td>Ash, wppm</td>
<td>0 - 450</td>
</tr>
<tr>
<td>Metals (As, Fe, Si, Ni, V), wppm</td>
<td>As (2 - 33), Fe (0.6 – 72), Si (1 – 25), Ni+V (0.7 – 7)</td>
</tr>
<tr>
<td>Chlorides, wppm</td>
<td>3 - 40</td>
</tr>
<tr>
<td>Bromine Number</td>
<td>30 – 60</td>
</tr>
<tr>
<td>Aromatics</td>
<td>as high as 90% Aromatics</td>
</tr>
<tr>
<td>Wide Distillation Range</td>
<td>30 – 640 °C</td>
</tr>
</tbody>
</table>
Shale Oil Production and Outlets

Raw Shale Oil needs to be stabilized and made suitable for transport (e.g. pour point for pipeline transport)

Syncrude or Finished Products:
- Nearby Refinery or refineries depending on volume
- Upgrader near Oil Producer - Can be a centralized Facility

Retort (Ex-Situ) or In-situ Extraction:
- A Chevron and Lummus Technologies Joint Venture

Finished Products – naphtha, diesel, jet, low sulfur fuel oil
## Upgrading Shale Oil – Technological Solutions

<table>
<thead>
<tr>
<th>Challenge</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large “tails” with excessive contaminant levels</td>
<td>Stabilize and properly fractionate prior to hydroprocessing.</td>
</tr>
<tr>
<td>Polymerization and gum formation</td>
<td>Use properly designed CLG Diolefins Saturation (DOS) reactors</td>
</tr>
<tr>
<td>Entrained solids (10-50 microns)</td>
<td>Use automatic backwash filters with CLG specified filtration rates</td>
</tr>
<tr>
<td>Microfine solids/ash</td>
<td>Use specialty filters after stabilization and proper distillation. e.g. Mott Filters</td>
</tr>
<tr>
<td>High Arsenic</td>
<td>High Nickel CLG Catalyst System</td>
</tr>
<tr>
<td>High Metals (Ni, Fe, V, Ca, Na)</td>
<td>High activity HDM catalysts with proper layering and distribution of pores</td>
</tr>
<tr>
<td>Excessive Pressure Drop</td>
<td>CLG UFR Technology - demonstrated worldwide in RDS technology</td>
</tr>
<tr>
<td>Chlorides and high TAN</td>
<td>Metallurgy, proper location of permanent and intermittent water washes</td>
</tr>
<tr>
<td>Large Heat Release and Temperature Maldistribution</td>
<td>Adequate quench capacity in RGC, proper bed height distribution, and use of ISOMIX-e internals</td>
</tr>
<tr>
<td>Retention of Naphtha, Jet, and Diesel Boiling range Material in Feed, minimize hydrogen consumption</td>
<td>Use CLG-patented “Split-Feed“ injection concept</td>
</tr>
<tr>
<td>Maximize Diesel Selectivity</td>
<td>Latest generation of mid-distillate selective catalysts with extremely low C4-production</td>
</tr>
<tr>
<td>Excessive Catalyst Deactivation</td>
<td>Use high hydrogen partial pressure</td>
</tr>
<tr>
<td>Frequent catalyst changeout</td>
<td>Use Chevron Modular Isolation technique</td>
</tr>
</tbody>
</table>
Commercial Shale Oil Upgrading
.... the early years

Southern Pacific Petroleum NL

- Commercialized a 1,700 BPSD Stuart Shale-derived naphtha hydrotreater
- Naphtha Hydrotreater Plant operated between 1999 and 2004
- Performance met expectations and over 900,000 barrels of C4-220°C naphtha were processed to meet specifications
- A Kerosene fraction was also produced and was certified for Jet A-1 specifications
- Basic engineering package was prepared for synthetic crude production for 220°C+ material. Pilot plant results validated results.
Shale Oil Upgrading - Commercialization

Design for Synthetic Crude Production Plant - Chevron Salt Lake City Refinery

99.7% of HDS and 99.0% of HDN achieved

Demetalization #1
(1100 psia H₂ pp)

Demetalization #2
(1100 psia H₂ pp)

Hydrotreater
(1850 psia H₂ pp)

Stabilizer

C₄⁻ and H₂S

13,845 BPSD
C₅⁺ Synthetic Crude

6,500 BPSD

6,500 BPSD

6,500 BPSD

13,000 BPSD

From Retort

API: 22
S: 5,800 wppm
N: 20,000 wppm
O: 12,000 wppm
Metals: 72 wppm

API: 24.5
S: 1,700 wppm
N: 18,600 wppm
O: 5,000 wppm
Metals: 2 wppm

API: 39.3
S: 15 wppm
N: 200 wppm
O: Nil
Metals: Nil

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Recent Upgrading Experiences

Since 2008, CLG has conducted several pilot plant campaigns with various feeds and configurations to produce Synthetic crude and final products.

- Feed pretreatment reactors to remove metals and olefins.
- Bulk hydrotreating to produce Synthetic Crude
- Bulk hydrotreating/hydrocracking with fractionator bottom recycle stream to make finished products (Jet, Euro V diesel)
- Spilt-feed hydrotreating/hydrocracking to maximize the production of middle distillates. (Jet, Euro V diesel)
Syncrude Production

- Only for Syncrude Production
- Simple Scheme
- Less Equipment Count
Finished Products – Low Capacity Units

- Smaller Unit Capacity (10,000 - 15,000 BPSD)
- Simple Scheme
- Less Equipment Count

C4 - Gases
Naphtha
Jet
Diesel
Low Sulfur Fuel Oil
Recycle Oil
Maximizing Mid-distillates – Higher Capacity Units

- Larger Unit Capacities (> 15,000 BPSD)
- Preserves Diesel Range Material in Feed
- Can Isolate Trains
- Processing Flexibility (feeds, products, quality)
- Minimizes Hydrogen Consumption
- Minimizes Total Reactor Volume
- Optimizes Reactor Operating Conditions

High Hydrogen Partial Pressure maintains proper liquid phase in reactors, reduces required operating temperatures, reduces catalyst deactivation dramatically, and produces highest quality products

- C4 - Gases
- Naphtha
- Jet
- Diesel
- Low Sulfur Fuel Oil
# Product Yield & Properties

<table>
<thead>
<tr>
<th>Synthetic Crude</th>
<th>Finished Products</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>API</strong></td>
<td>~ 30</td>
</tr>
<tr>
<td>Sulfur, wppm</td>
<td>100 - 500</td>
</tr>
<tr>
<td>Nitrogen, wppm</td>
<td>500 - 1000</td>
</tr>
<tr>
<td>Naphtha, LV%</td>
<td>10 - 20</td>
</tr>
<tr>
<td>Naphtha Sulfur, wppm</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>N + A. LV%</td>
<td>&gt; 50</td>
</tr>
<tr>
<td>Jet, LV%</td>
<td>10 - 20</td>
</tr>
<tr>
<td>Jet Smoke, mm</td>
<td>&gt; 25</td>
</tr>
<tr>
<td>Mid-distillate, LV%</td>
<td>70 - 90</td>
</tr>
<tr>
<td>Diesel, API</td>
<td>~ 39</td>
</tr>
<tr>
<td>Diesel, Cetane Index</td>
<td>&gt; 55</td>
</tr>
<tr>
<td>Diesel, Sulfur, wppm</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Diesel, CFPP, °C</td>
<td>&lt; -20</td>
</tr>
<tr>
<td>Low Sulfur Fuel Oil, Sulfur, wppm</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>
What your product will look like!
Summary

- CLG showed you several commercially viable upgrading options.
- CLG will work with any shale oil producer and tailor a solution that is appropriate for the site, nature of the oil, and the potential product outlets.
- CLG patented split-feed technology (6 operating, 10 in EPC) maximizes diesel yield and minimizes hydrogen consumption and is the preferred technology for larger capacity upgraders.
- CLG recommends very careful feed analysis for addressing both catalytic and operational issues.
- Fifty years of hydroprocessing difficult feeds has proved the advantages of high hydrogen partial pressures for building robust units.
- CLG patented reactor systems such as the UFR are critical components in achieving high operating factor.
Thank you!

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