High Conversion of Vacuum Residue

Opportunities and Challenges

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Cost of Doing Nothing Post 2020

- For a 300,000 bpsd refinery post 2020, the opportunity cost of Not Upgrading the VR will be over $500 million/year!

- Blending to produce ULSFO will permit refinery to continue operation; high value ULSD or FCC feed at several times the volume of VR (6 to 9 times) will be needed to make 0.5 wt.% Sulfur FO for high sulfur Middle Eastern VR

- Sweet Crudes will cost at least $2/bbl more or roughly a $220 million/year penalty! Limited supply and refiner has to change product pattern.
Market Pressures Driving Residue Upgrading Solutions to High Conversion

- Worldwide transportation fuel demand is increasing relative to heavy fuel oil or coke.
- Petchem demand > Transportation Fuels >> HSFO
- Relative product prices support high conversion of residue
- Push for more Chemicals Production from Crude to increase margins

Challenge is to find high conversion solutions based on proven low risk technologies
Which Residue Upgrading Approach to Take?

- **Coking**
  - Full Conversion
  - High feed flexibility
  - Doesn’t make LSFO
  - Lower liquid yields and Coke disposition

- **Residue Hydrotreating**
  - Can make LSFO
  - Feedstock considerations
  - Combine with RFCC to make gasoline

- **Residue Hydrocracking**
  - 60 - 97+ % conversion
  - Feed flexibility
  - Highest liquid yields
  - LSFO possibilities
Residue Conversion High Conversion Solutions Are All Available through CLG/MDR

- Crude Unit
  - Naphtha Distillates
  - Hdt VGO/DAO/AR
  - VGO
  - Hdt VGO/DAO/AR
  - UCO
  - Refinery Light Streams

- Vacuum Unit
  - AR
  - VR
  - LC-FINING LC-MAX LC-SLURRY
  - New Sat. Gas Plant
  - Delayed Coking
  - SDA
  - DAO
  - Pitch
  - Coke

- ISOTREATING
  - Sat. Gas Plant
  - Hdt Naphtha
  - Jet, Euro V Diesel
  - Hdt Naphtha
  - Jet, Euro V Diesel

- ISOCRACKING
  - (R)FCC/INDMAX
  - FCC Naphtha HDS
  - H2S
  - NH3
  - H2, Syngas Power, Steam

- Hydrogen Plant
  - LPG
  - H2 Rich Gas
  - Sulfur Recovery
  - Fuel Gas
  - Sulfur
  - H2, Syngas Power, Steam

- Hydrogen Recovery
  - E-GAS

- Gasoline Block
  - Methanol
  - Ethanol
  - MTBE
  - ETBE
  - ISOMPLUS
  - TAME
  - TAEE

Legend:
- CLG
- MDR
- Others
Highest Boiling Fragments Are Very Polar and Very Rich in HPNA

Figure 2.7  The effect of molecular weight and structure on boiling point.

Courtesy: Irvin A. Wiehe
CCR to Diesel – Hydrogen Consumption

- CCR has ~ 3.8 wt % hydrogen
- Euro V Diesel requires 14.5 wt % hydrogen to meet S.G. specifications; Petrochemical Naphtha has 15.5 wt.% Hydrogen.
- In order to convert 25 wt % CCR in VR to Diesel or Naphtha, we will require an increment of 10.7 to 11.7 wt % hydrogen! This will not be economically viable under most scenarios.
- Smart CCR conversion is key to residue hydrocracking
Robust LC-FINING Ebullated Bed Residue Hydrocracking Technology Platform

- **Catalyst Addition Line**
- **Density Detector**
- **Radiation Source Well**
- **Effluent**
- **Thermowell**
- **Nozzle**
- **Normal Bed Level**
- **Expanded Catalyst Bed, No DP**
- **Skin TC’s**
- **Catalyst Withdrawal Line**
- **Feed**
- **Recycle Pump**

**Specifications:**

- **Reactor Temperature:** 410 - 440 °C (770 - 824 °F)
- **Reactor Pressure:** 110 - 180 bar (1600 - 2600 psig)
- **Resid Conversion:** 55 - 80 %
- **Hydrogen P.P.:** 75 - 125 bar (1100 - 1800 psi)
- **Chem H₂ Consumption:** 135 - 300 Nm³/m³ (800 - 1780 SCFB)
- **Desulfurization:** 60 - 85 %
- **CCR Reduction:** 40 - 70 %
- **Demetallization:** 65 - 88 %
Can result in significant HSFO reduction and LSFO production with certain feeds
LC-FINING with Integrated Hydrotreating Produces Clean High Quality Products

Hydrotreating costs reduced 40 - 50 %
LC-FINING with Integrated Two-Stage Hydrocracking Maximizes High Value Distillates

Key is a “clean” second-stage and VGO End Point Control
Shell Canada

Integrated Hydrotreater

LC-FINING Reactors
Neste Porvoo, LC-FINING With Integrated ISOCRACKING Facility to Make Euro V Compliant Naphtha and Diesel
Residue Hydrocracking Challenges

- Conversion restricted by the nature of feed
- Sediment formation rises rapidly at higher conversions; conversion often limited by back-end fouling
- Full reactor potential (capital utilization) often restricted by sediment in UCO
- Hydrogen is wasted in hydrogenation and hydrocracking of heavy asphaltenes
- Selectivity to liquid decreases at high temperature required for conversion. Hydrogen wasted in making low value C\textsubscript{4}- material.
LC-MAX – Block Flow Diagram

- Vacuum Resid Feed
- First LC-MAX Reaction Stage
  - Make-up $H_2$
  - HP/HT Separator
  - Atmospheric Fractionator
  - Gas Cooling Purification & Compression
  - $H_2$ Rich Treat Gas
- Second LC-MAX Reaction Stage
- Gas Cooling
- Purification & Compression
- DAO
- Vacuum Residue
- Vacuum Distillates
- Atmospheric Distillates
- Solvent Deasphalter
  - 75 - 80 % Lift
  - Pitch to Gasifier/ Coker/CFB

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LC-MAX – Process Features

- 90 %+ conversion for difficult crudes
- Fully integrated two-stage process
- Whole VR is hydrocracked in a first reaction stage
- Stage 1 UCO is deasphalted to remove heavy asphaltenes
- DAO is hydrocracked in Stage 2 (*much higher rate constant and cleaner operation*)
- Hydrogen not wasted in hydroconversion of difficult heavy asphaltenes (*hydroconversion of heavy asphaltenes produces 4-ring HPNA that are very difficult to upgrade*)
## LC-MAX vs. LC-FINING for Ural VR

<table>
<thead>
<tr>
<th>Feature</th>
<th>LC-FINING</th>
<th>LC-MAX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion, %</td>
<td>63</td>
<td>88 - 92</td>
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<tr>
<td>Feed Flexibility</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Reactor Volume</td>
<td>Base</td>
<td>0.9 x Base</td>
</tr>
<tr>
<td>Chemical Hydrogen</td>
<td>Base</td>
<td>Base x 1.15 for 20 % Higher Conversion</td>
</tr>
<tr>
<td>Catalyst Addition Rate</td>
<td>Base</td>
<td>Base x 0.88</td>
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<tr>
<td>Bottoms Product</td>
<td>LSFO</td>
<td>Coker Feed, Gasifier Feed</td>
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<tr>
<td>Fractionation Section Fouling</td>
<td>Base</td>
<td>&lt;&lt; Base</td>
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<tr>
<td>Unconverted Oil Disposition</td>
<td>LSFO</td>
<td>Gasifier Feed, CFB, Power Plant</td>
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Significant Yield Increase With LC-MAX

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Base</th>
<th>+10.3</th>
<th>+17.3</th>
<th>+21.7</th>
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<tbody>
<tr>
<td>C1-C4</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Naphtha</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Diesel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VGO + DAO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coke/Pitch</td>
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85 wt % Liquid Products

90+ wt % Conversion
LC-LSFO TO MEET IMO 2020
What is LC-LSFO?

- A Process for upgrading LC-FINING High Sulfur Unconverted Oil to Low Sulfur Unconverted Oil

- LC-LSFO objective is to produce low sulfur oil from LC-FINING Unconverted Oil

- LC-LSFO is suitable for LC-FINING ATB (Atmospheric Tower Bottom) or heavier VTB (Vacuum Tower Bottom).

- LC-LSFO treated residue can meet 0.5 wt % sulfur and blended to Low Sulfur Fuel Oil.
Minimum modification required as recycle gas flow increase is negligible

- LC-FINING flow scheme remains unchanged
- Add new filtration on ATB or VTB
- Add new HOT Reactor, Furnace, HP Feed Pump, HPHT, MPHT, Product Stripper or Product Fractionator
Near 100% conversion of heavy oils / SDA tar to high-value products

- 115% liquid yield
- Over 80 vol % Euro V diesel (after VGO HC)

Unique high activity catalyst
- Recovered in the process
- Eliminates fouling concerns associated with other catalyst or additive systems

Based on LC-FINING platform
- Commercially proven and reliable
- Optimal reactor configuration
The Early Years of Slurry Hydrocracking Development

1978-1984: Chevron started slurry hydrocracking work in late ‘70’s. Simple Fe-based Additives tested followed by Mo-based Additives. Technology used Bubble Reactors. Parallel work on Coal Liquefaction carried by both Chevron and Lummus. Oil shock of 1979 and a period of high oil prices led to decision to build 16 TPD demo plant in Richmond refinery in 1984. Unit ran for 6 months and generated a lot of data. Shutdown to secure tax credits for Chevron that funded work.

1984 – Chevron merges with Gulf. Gulf Research had developed high activity Mo.-catalyst.

  - Used special Mo.-catalyst (nano catalyst)
  - Conversion achieved 95 - 99 %.
  - Work stopped because of severe budget constraints in refining industry

1999-2001: Chevron acquires partial ownership of AOSP Project Edmonton Canada. AOSP (Shell Canada) builds large LC-FINING unit. Chevron sees advantage of LC-FINING platform compared to Bubble Reactor Platform.


2002 – Scale-up Risk of Reactor Technology Evaluated. Texaco and Chevron experience with EB Technology leads to selection of Liquid Circulation (LC-FINING) Platform instead of Slurry Bubble Column for all future work.
Intense R&D and Commercialization

- **2003** – Slurry Hydrocracking Research Program restarted with intense focus on Upstream Upgrading. Scale-up of catalyst synthesis, resid hydrocracking, solids separation and metals recovery. Name Changed to Vacuum Residue Slurry Hydrocracking (VRSH) to reflect new catalyst and process platform
  
  ▶ Extensive Work on Very Heavy VR feedstocks (e.g. Hamaca & Maya)
  
  ▶ Integrated HDT, first commercialized in LC-FINING units, used for High Quality Products

- **2005** – Decision to construct 600 TPD-protype in Pascagoula Refinery. Project funded through Engineering and Procurement.

- **2007** – Large pilot plant RU-87 (175 kg/day) commissioned in Richmond to supplement smaller pilot plants (RU-85 and RU-86). Earlier VRSH testing carried out in Lummus’ large pilot facilities in Bloomfield.

- **2008-2009** Large Catalyst Deoiling Plant built in Richmond. Large Scale Catalyst Synthesis and Metals Recovery Demonstrated

- **2010** – Chevron cancels construction of prototype because of sharp drop in Crude Oil prices and explosive growth of light shale oil crude oil. Upstream interest lost.

- **2012** – Research effort restarted with focus on downstream applications (for refineries). Bimetallic Catalyst developed. Very long runs with most difficult feeds demonstrated. Next generation catalysts developed.

- **2015** – VRSH rolled into CLG for licensing. Name changed to LC-SLURRY

- **2016** – Major Oil Companies express interest in LC-SLURRY. CLG licenses first LC-SLURRY unit to Beowulf / Preem who had earlier evaluated VCC for nearly two years.

  **CLG Licenses the first LC-SLURRY Unit For Beowulf / Preem in Sweden. This 2.5 MM MTA unit will produce Euro V Diesel and LSFO (< 0.5 wt.% Sulfur).**
LC-SLURRY
Optimal Flow Scheme for Slurry Hydrocracking

Catalytic performance optimized via reactors in series and recycle

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What is LC-SLURRY?

<table>
<thead>
<tr>
<th>Unit</th>
<th>Description</th>
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| RHS – Residue Hydrocracking Section | Slurry resid hydrocracking unit  
• Achieves full (97%+) VR conversion  
• Uses ISOSLURRY catalyst  
• Based on LC-FINING reactor platform |
| CDS – Catalyst Deoiling Section | Process to separate spent VRSH catalyst from the unconverted oil             |
| CSS – Catalyst Synthesis Section | Prepares ISOSLURRY catalyst from Ni and Mo Salts                           |
| MRU – Metals Recovery Unit   | Process to recover metals from spent ISOSLURRY catalyst (outside facility- not part of plant) |
LC-SLURRY
Maximizes Valuable Products

- C₄- (wt %) Fuel or Hydrogen Plant Feed
- Hydrotreated Naphtha Can send HN to CCR
- Diesel Euro V Quality
- Hydrotreated VGO Can send direct to FCC or HC
- Heavy Oil, Solids-free to LSFO, Coker or FCC

Zero residue is produced!
LC-SLURRY – Makes Over 81 Vol % Diesel After VGO HC and Heavy Oil Processing

- C4- (wt%)
- Naphtha
- Euro V Diesel
- VGO+

Liquid Volume %

<table>
<thead>
<tr>
<th></th>
<th>LC-SLURRY</th>
<th>LC-SLURRY + VGO HC &amp; HO Processing</th>
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<tbody>
<tr>
<td>Naphtha</td>
<td>67</td>
<td>81</td>
</tr>
<tr>
<td>Euro V Diesel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VGO+</td>
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</tr>
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LC-SLURRY
Differentiated by Several Key Components

- **ISOSLURRY™ Catalyst**
  - Highly active, ultra-fine, proprietary bimetallic catalyst
  - Produced and activated ex-situ

- **Hydrocracking Section**
  - LC-FINING proven reactor platform
  - Multi-stage reactor system

- **Hydroprocessing Section**
  - In-line hydrotreating removes contaminants
  - Additional hydroprocessing can increase Euro V Diesel production and allow heavy oil product to be blended to LSFO or processed in Coker / FCC

- **Catalyst / Oil Separation**
  - Re-adapted, proven technology effectively recovers the catalyst from bottoms oil
  - Enables use of bottoms stream for coker feed, fuel oil etc.
  - Spent catalyst rich in metals and suitable for metals recovery
ISOSLURRY™ Catalyst
Designed for Superior Performance

- Based on residue hydroprocessing catalyst know-how
- Unique and optimized properties
- Highly active nickel moly-based catalyst
- Excellent access to reactive sites
- Produced ex-situ to ensure high quality

- Catalyst quality and dosage
  - Keeps the system clean
  - Suppresses coke formation
  - Improves bottom oil quality
  - Allows very high conversion with reliable operation
LC-SLURRY
Upgrades the Most Difficult Molecules

- MCR/CCR conversion tracks VR conversion
  - Avoids instability issues
  - Avoids large coke make
  - 94% HDMCR and 97% VR conversion on SDA tar

- Catalyst quality and dosage
  - Keeps the system clean
  - Suppresses coke formation
  - Improves bottom oil quality
  - Allows very high conversion with reliable operation
CLG Offers All Residue Upgrading Technologies

- Commercially Proven
- High Liquid Yields
- Meets or Exceeds Future Specifications
- Maximizes Feed and Product Flexibility
- Low or Zero Residue