Catalytic Solutions for Increasing Middle Distillate Yields –
Resid Hydrocracking and Post Hydrotreating Synergy

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Agenda

• Introduction to ART

• Market Sentiment and Drivers

• Ebullated Bed Resid Hydrocracking (EB RHC) Catalyst
  • New Catalyst Technology - ECAD™

• Straight Run vs. EB RHC Products

• Characterization of EB Resid VGO

• Hydrotreating Options for EB Resid VGO

• Summary
Who is ART?

• A 50/50 Joint Venture, formed in 2001, between Chevron and Grace
• Global technology and market leader in Hydroprocessing Catalysts to meet the clean fuels challenges of refiners
• Exclusive Partner of CLG for Fixed Bed Resid, Ebullating Bed, Hydrocracking and Lubes catalysts
• Fully integrated technical support teams
• Delivering real value to our customers
A Full Spectrum of Solutions

Resid Hydroprocessing
- Fixed Bed Resid (FBR) Systems
- Up Flow Reactor (UFR®) and
- On-Stream Catalyst Replacement (OCR®) Systems
- Ebullating Bed Resid (EBR) Systems

Hydrocracking
- ISOCRACKING® Catalyst System

Lubes Production
- ISODEWAXING® Catalyst System
- ISOFINISHING® Catalyst System

Distillate Hydrotreating
- For silica tolerance: StART® Catalyst System
- For sulfur minimization: SmART Catalyst System®
- For advanced pretreating: ApART® Catalyst System
• Driven by the availability of more heavy/sour crudes

• High recent activity for new EB RHC projects – high ROI

• Catalyst technology is playing an ever stronger role

• Maximizing conversions at minimum sediment; longer on stream availability with lowest catalyst costs per barrel of feed

• Post processing of the VGO derived from the EB RHC, careful review and the right catalyst options to maximize profitability
EB Technology Customer Needs – Catalyst Standpoint

- **High Resid Conversion**
  - To Distillate (preferably) and VGO
- **Low Sediment in Reactor Effluent**
  - Lower downstream fouling (max run lengths)
  - Lower inherent coking in reaction circuit
- **High HDS Activity**
  - Lower sulfur in bottoms for fuel oil
  - Lower sulfur in Distillate and VGO

- **Good MCR conversion**
  - Important for units sending HT bottoms to Cokers or for synthetic crude production
- **Highest possible HDN for lowest N in all converted products**
  - Strong impact for the VGO feed to FCC
- **Lowest cost ($/bbl of feed processed)**

**Feedstock**

- Vacuum Resid
- Atmospheric Resid
- Coker Gas Oil
- FCC Bottoms
- Bitumen (Tar Sands)

**Key Products**

- LPG
- Naphtha
- Distillate
- Gas Oil
- Low Sulfur Fuel Oil/Coker Feed
- Synthetic Crude Blend
**ART’s EB Catalyst Technology Platforms**

- **Catalytic Activity**
- **Metals Capacity**

<table>
<thead>
<tr>
<th>Platform</th>
<th>Catalysts</th>
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<tbody>
<tr>
<td>DCS</td>
<td>GR-611</td>
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<tr>
<td>ECAD</td>
<td>GR-955</td>
</tr>
<tr>
<td>HSLS</td>
<td>GR-822, GR-823</td>
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<tr>
<td>LS</td>
<td>GR-LS10</td>
</tr>
<tr>
<td>HCRC</td>
<td>GR-737</td>
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</tbody>
</table>

- Flexibility to Customize Support Properties and Metals Functions
- Catalyst Systems Optimized For Different Feeds

**Catalysts in all five platforms can be tailor made to meet diverse and changing needs**
ART’s EB Catalyst Technology Platforms – Current Offerings, Including ECAD™

ECAD™ Bridges the Gap in Metals Capacity

- With Relatively Small Impact on Catalytic Activity Compared to the HSLS Platform
ECAD (Enhanced Catalytic Activity DeMet) Technology – **NEW**

- Development based on customer feedback and commercial success of dual catalyst systems
- Two years of high intensity research and development
  - *Initial results indicate ECAD is an alternative to current catalyst technologies in the 1st Stage of Dual Catalyst Systems, with the following key features:*
    - **Metals capacity between DeMet and HSLS Platforms**
    - **Catalytic activity higher than DeMet and similar to HSLS**
    - **Physical properties better than DeMet and equivalent to other Catalyst Technology Platforms**
ART’s EB Catalyst Technology – Single and Dual Catalyst System

DCS

HSLS

HSLS

HSLS

LS

LS

HCRC

LS

Commercial

Commercial Trials
ART’s EB Catalyst Technology - System Evolution

Continuous Catalyst Developments Leads to Step-out Performance Benefits

Conversion-Sediment Tradeoff Pattern

- LS/LS (2012)
- HSLS/LS (2012)
- HSLS/LS (2016)
- ECAD/LS (2016)

LS ➔
HSLS/LS
>30% Reduction

HSLS/LS ➔
ECAD/LS
>30% Reduction

Sediment, ppm
VR (579°C+) Conversion

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Impact of Catalyst Technology on Product Selectivity

### Product Selectivity

<table>
<thead>
<tr>
<th>Product</th>
<th>Condition 1</th>
<th>Condition 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kerosene (143-279°C)</td>
<td>10.0%</td>
<td>15.0%</td>
</tr>
<tr>
<td>Diesel (279-366°C)</td>
<td>15.0%</td>
<td>20.0%</td>
</tr>
<tr>
<td>LVGO (366-454°C)</td>
<td>20.0%</td>
<td>25.0%</td>
</tr>
<tr>
<td>HVGO (454-579°C)</td>
<td>30.0%</td>
<td>35.0%</td>
</tr>
</tbody>
</table>

**Catalyst Systems and Operating Severity both impact EB Products selectivity**
Differences between EB RHC and Standard VGO

- Major difference in cycloparaffin and tetraaromatic content between SR VGO and EB VGO
- Almost no tetraaromatics in SR VGO
- Much higher thiophenic sulfur in EB RHC VGO
What makes feeds refractory?
Let’s talk Double Bond Equivalent (DBE)

Light VGO (467-495 °C BP)

Heavy VGO (500-525 °C BP)

VR (579-605 °C BP)

DBE = \( \frac{2C - H + N + 2}{2} \)

DBE = # rings + # double bonds

# H₂ molecules needed to reach full saturation
EB Resid VGO More Highly Aromatic Than RDS VGO

\[ DBE = \frac{(2C - H + N + 2)}{2} \]

dicates the S-, N-free part of aromatics fraction

**APPI Mass Spectrometry to Identify Refractory Aromatics**
Truncation at \(~480 \, ^\circ\text{C}\) limits Resid Entrainment HPNA’s to Coronene

**Grain Graphs**

- **Left Graph:** LC - FINING VGO
- **Right Graph:** Truncated LC - FINING VGO

**Graphs** represent S-, N-free part of aromatics fraction
EB Resid Unit With Integrated Hydrocracker
Design Objectives for Integrated ISOCRACKING Unit for EB Resid Gas Oils

- Increased conversion to ~80 vol % of EB resid-derived VGO
- Maximum Euro V diesel yield
- Diesel Sulfur <10 wppm
- Diesel Cetane Number > 51
- Diesel Aromatics <20 Wt %
- Naphtha Nitrogen <0.5 wppm
Optimized Partial Conversion ISOCRACKING

HPNA’s from Opportunity VGO accumulate in recycle stream
ICR 1000 Series

ICR1001 preferentially equilibrates HPNA

Traditional Catalysts preferentially convert VGO

Lowers Bleed Rate through faster HPNA Equilibration
ICR 1000 is HPNA Cleanser

Graphs represent S-, N-free part of aromatics fraction
High Conversion of RHC VGO Learnings

- EB resid-derived gas oils can be readily desulfurized and denitrified to <10 ppm
- HPNA’s strongly affect cracking reactivity and cycle length
  - EB VGO end point and sharpness - important in determining conversion and deactivation rate
  - Decreasing the EP from 482°C to 468 °C reduced deactivation rate by a factor of 5
  - Increasing hydrogen partial pressure from 124 to 145 bar reduces fouling rate by a factor >30
  - Even a 25°C increase in EP can increase fouling rate by a factor of 10
- A “clean” second stage is needed to obtain high conversions with reasonable cycle length
- Right catalyst choice and conversion levels in reactor stages is critical
Summary

- New ECAD™ Catalyst Technology fills the gap between the DeMet and Conversion catalyst platforms

- Dual Catalyst Systems, offer a high degree of synergy - *Maximum $/bbl upgrade value*

- Catalyst Technology along with the unit operation severity impacts the selectivity and quality of the EB RHC products

- Extensive work in speciation at ART labs has allowed providing catalyst and process solutions for handling the heavy products from the EB RHC process

- ART’s superior catalyst technology, advanced technical support and its leverage of Grace, CLG and Chevron *‘drive and deliver the value’* to achieve high profitability
Thank You

When you’re ready for a better perspective on hydroprocessing solutions, we’d like to start a conversation.

Questions?

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