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Hiro Toshima worked for ExxonMobil Japan for 17 years and joined Albemarle Corporation (ex. Akzo Nobel) in 2004. Hiro’s specialty spreads wide range of process and catalyst developments in the petroleum refining industry. He is now in charge of Resid Hydroprocessing technologies, and is involved in the technology and business developments. He resides in the Netherlands with his family to work in the Amsterdam marketing headquarter.

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ENHANCED E-BED BOTTOMS UPGRADING
USING LATEST CATALYTIC TECHNOLOGY

H. Toshima, S. Mayo, Z. Sedlacek, T. Hughes, and M. de Wind
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The heavy-oil upgrading impacts very much on the refinery profitability with the possible parameters of crude and product prices, conversion, yields, volume swell, and quality of the products. The Ebullated-bed process is one of the solutions for the effective primary upgrading with the heavy oils. Albemarle commercialized several E-bed catalysts since the 1970’s for the bottoms upgrading in low sediment and high hydrogenation operations.

The E-bed plant operation is focused on maximizing the VR conversion and throughput while keeping a certain product specification. However, frequently conversion increase is limited by the fouling problem caused primarily by the sediment in the product. Albemarle has tackled this tough subject through thoroughly characterizing the asphaltenes and sediments for in-depth understanding of oil chemistry and compatibility. With such deeper understanding, Albemarle succeeded in developing the improved E-bed catalytic technologies to extremely reduce the sedimentation in the products. The latest development involves both the patented catalyst-staging technology and the improved single catalyst application. Those technologies can achieve extremely low sediment and/or a higher HDS and CCR removal for greater bottom upgrading.

The author will present the oil chemistry and its based catalytic technology developed for the improved E-bed process performance.
Enhanced E-bed Bottoms Upgrading Using Latest Catalytic Technology

5th NCUT Upgrading and Refining Conference 2009

Business Drivers for Bottoms Upgrading

- **Increasing Sour and Heavier Crudes**
- **Growing Unconventional Crudes**
- **Changing Product Demands**
  - Dieselization
  - Lower Fuel Oil Demand
- **Growing Imbalance of Fuel Oil Demand and VR Production**
- **Economic Incentives**
- **MARPOL Annex VI Revision**
Increasing E-Bed Capacity

- **EBR (Ebullated-Bed Resid) process capacity has been extensively increased since the mid 1980’s**
- **Canada has the biggest EBR capacity**

*Throughput basis incl. planned revamping and new units*
Albemarle’s Vision for Heavy Oil Upgrading

- Albemarle will be the leader in emerging heavy oil fuels technologies
  - Leverage cutting-edge catalytic technologies for Oil Sands Bitumen upgrading in Canada
    - EBR and FBR Catalytic Technologies for Primary Upgrading
    - STARS™ and Nebula® Catalytic Technologies for Secondary Upgrading
EBR Fouling Mechanism

- Fouling in EBR units is predominantly caused by formation of a mesophase (asphaltene aggregate)
  - Foulants; Ash=5-20wt%, H/C=0.62-0.75, fa=0.84-0.94, MW=500-2,500, WAX molecular stacking parameters $d_{002}/L_{C002}=3.5\AA/60\AA$

- Controlling this mesophase formation is key

<table>
<thead>
<tr>
<th>Polarized-light Microscopy (micron order)</th>
<th>SEM (sub-micron)</th>
<th>WAX (angstrom)</th>
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<tbody>
<tr>
<td>(a) Asphaltene in Product</td>
<td>(b) Foulant</td>
<td>(c) Foulant</td>
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<tr>
<td>(d) Molecular Stacking Model</td>
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Asphaltene Management

- Perform detailed characterization of the asphaltene molecules in the reactor
- Incorporate molecular structures into a database for catalytic design to reduce asphaltene and sediment
Albemarle’s EBR Catalyst Portfolio

Commercially Proven Sediment Reduction Technology

- Activity (HDS, HDCCR)
- Asphaltene Cracking
- Sediment Quantity

Bar chart showing performance metrics for KF 1310, KF 1311, KF 1312, and Catalytic Staging.
Value of Sediment Reduction Technology

• Higher Conversion and/or More Barrels
  – Higher conversion by up to 10 vol%
  – Margin increase by $10 – 20 million p.a. (@30kbd)

• Replacing Diluent by More VR-intake

• Extended Cycle Length

• Reduced Heat-Exchanger and Towers Cleaning Cost

• Reduced CAR (Catalyst Addition Rate)
Latest EBR Needs and Catalyst Development

• Recent industry operations favor higher CCR and Sulfur removal as well as improved sediment reduction

• Albemarle has been developing new EBR catalyst technologies for higher HDCCR and HDS while further improving HDM and sediment reduction capacity

  – The first target is even lower sediment formation in severe operations with heavier and higher metals feedstocks

  – The second target is higher HDCCR and HDS with constant low sediment formation
Albemarle’s Catalyst Development Protocol

**Catalyst Testing and Modeling**
- Testing with streamlined pilot capacity
- Activity and stability
- Pore plugging
- Accessibility and stability
- Reactor kinetic model

**Feed Characterization**
- Feed source, diluent
- Distillation
- Contaminants (S, N, CCR, Ni, V, Na, Fe, Ca, Si, As)
- SARA composition
- MW distribution

**Catalyst Design**
- Component/molecule focus
- Pore architecture
- Surface activity
- Accessibility and stability

**Process Conditions**
- Process objectives
- P, T, scf/bbl, lhsv, recycles, CAR
- Catalytic/Thermal ratio
- Spent catalyst properties
Catalyst Development Protocol

Feed Characterization
- Distillation
- Contaminants
- SARA composition
- MW distribution

Catalyst Design and Testing
- Focus on specific components/molecules for performance selectivity
- Pore architecture and surface activity
- Testing with streamlined capacity
- Pore plugging, deactivation and accessibility
- Reactor kinetic modeling

Different VR-feeds

fraction

log (molecular size)

V-deposition in Extrudate
Catalyst Effective, Factor 0.6
Development Approach

- **Sediment Reduction**
  - More focus on Asphaltene diffusion and reaction
  - Controlled hydrogenation for better oil compatibility

- **CCR and Sulfur Removal**
  - HDCCR and HDS improvements target primarily on Aromatics and Resin components
New Catalyst Development

- KF 1316 for Lowest Sediment Formation
Improved Oil Compatibility

- HDS (HDCCCR) and sediment reduction is a trade-off
- State-of-the-art pore architecture in KF 1312 and KF 1316 results in better performance selectivity
Summary of New Developments

- **KF 1312 – Strong Sediment Control Catalyst**
  - Improved HDAsp and sediment reduction
  - Valuable tool for heavy and high metals crudes, higher conversion-barrels, and longer cycle length
  - Proven successful commercial track record

- **KF 1316 – New Generation Sediment Control Catalyst**
  - Custom designed pore architecture and surface activity
  - Further enhanced HDAsp for lowest sediment formation
  - Extremely robust tool for processing much heavier and higher metals crudes in high severity operations
  - Higher conversion-barrels
  - Longer cycle length
  - Robustness for crude slate changes
Conclusions

- Canada is a leading country in commercial EBR upgrading
- Albemarle’s cutting-edge catalyst technologies help leverage Canadian Oil Sands Bitumen upgrading
- Albemarle has continuously developed a variety of improved EBR catalyst technologies
  - KF 1312 – Strong Tool for Sediment Control
  - KF 1316 – New Generation Sediment Control Catalyst
  - New Generation HDCCCR/HDS Catalyst – Will be emerged soon
- Albemarle is able to tailor EBR catalysts for customer specific needs utilizing our state-of-the-art catalyst design strategies