ADVANCES IN REFORMING CATALYST

International Refining Seminar
“Refining Challenges and Way Forward”
Organised by Petroleum Federation of India
16th -17th April, 2012
New Delhi (India)

Mohan Lal
Axens India
March 2011 Acquisition of the reforming business of Criterion corporation

- Each Heritage catalyst produced within heritage organization
- On-going cross production trials
  - Different paths lead to quality products: mechanical strength, hydrothermal stability, chlorine retention
  - Great improvement potential from experience sharing
• Current situation
  • Axens & Criterion legacy products still available

• On going process for
  • Portfolio consolidation
  • New products launching
What do Customers Look For?

Customer Targets

• Proven and reliable catalyst

• Improved economics
  • Low cost-to-fill
  • High hydrogen & Reformate production or aromatics production

• Low operating cost

• High Stability

Axens’ Solutions

➢ Homologated by Majors

➢ More than 200 references with promoted catalyst

➢ Optimal Pt content & Loading density

➢ Minimised side reactions
  Use of promoted catalyst

➢ High chloride retention

➢ High mechanical resistance

➢ Stable surface area

➢ Stable platinum dispersion

➢ Low coke make catalyst
Fixed Bed Reforming Catalysts
SR & Cyclic section

- Current portfolio
- New products
- Development
- Summary
- Reactor technology
### Fixed Bed Reforming Catalysts Established Products

#### The largest family of Multi-Promoted Fixed Bed Catalysts

<table>
<thead>
<tr>
<th>Re / Pt</th>
<th>0</th>
<th>1</th>
<th>1.3</th>
<th>1.6</th>
<th>1.8</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Target Unit</strong></td>
<td>CY</td>
<td>SR/CY</td>
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<td>SR</td>
<td>SR</td>
</tr>
<tr>
<td><strong>Increased Stability</strong></td>
<td>![Red Arrow]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Better S tolerance</strong></td>
<td></td>
<td>![Blue Arrow]</td>
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<td></td>
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</tr>
<tr>
<td><strong>Unconstrained Unit</strong></td>
<td>RG 532</td>
<td>RG 582</td>
<td>RG 682</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Increased Activity</strong></td>
<td>P 15</td>
<td>PR 15</td>
<td></td>
<td></td>
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</tr>
<tr>
<td><strong>Higher Density</strong></td>
<td></td>
<td>RG 586</td>
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- **Re / Pt** represents the ratio of rhodium to platinum in the catalysts.
- **Target Unit** indicates the type of reactor configuration.
- **Increased Stability** and **Better S tolerance** highlight the performance benefits.
- **Unconstrained Unit** lists the specific catalysts available.
- **Increased Activity** and **Higher Density** are additional features of the catalysts.
### Fixed Bed Reforming Catalysts New Products

**The largest family of Multi-Promoted Fixed Bed Catalysts**

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- **Increased Stability**
- **Better S tolerance**

**Unconstrained Unit**

- **Increased Activity**
- **Higher Density**

**New Products**
- PR 33
- PR 36
Fixed Bed Reforming Catalysts Available Products

The largest family of *Multi-Promoted* Fixed Bed Catalysts

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- **Increased Stability**
- **Better S tolerance**

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<td><strong>Higher Density</strong></td>
<td>RG 586</td>
<td>PR 36</td>
<td>PR 30</td>
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New

New
• Current portfolio

• New products

• Development

• Summary

• Reactor technology
New Reforming Catalysts

- Higher catalyst stability

P/N/A = 60/24/13 % wt
New Reforming Catalysts

- Higher yields stability

P/N/A = 60/24/13 % wt
**Outcome**

- The PR 33 & PR 36 catalysts provide
  - High catalyst performances
    - *Selectivity & stability*
    - *Fully regenerable*
  - At the lowest precious metal content
  - The highest NPV for fixed bed application
• Current portfolio
• New products
• Development
• Summary
• Reactor technology
Nearing Commercialization

- The highest selectivity with a maximum $C_8$ aromatics production at constant catalyst activity
The new family of multipromoted catalyst

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- Increased stability
- Better S tolerance
- Higher density

We call them PR as we initially focus on high density carrier
New Series Balanced version

Same activity but higher stability
20 % less coke
New Series
Balanced version

Normalized $C_5^+$, wt %

Time (hours)

Max selectivity catalyst

<table>
<thead>
<tr>
<th></th>
<th>PR 15</th>
<th>New</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>Base</td>
<td>+0.1</td>
</tr>
<tr>
<td>(wt %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_2$</td>
<td>Base</td>
<td>+60</td>
</tr>
<tr>
<td>(scfb)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_5^+$</td>
<td>Base</td>
<td>+1.5</td>
</tr>
<tr>
<td>(wt %)</td>
<td></td>
<td></td>
</tr>
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</table>
Higher C₈ aromatics yield catalyst
Axens Fixed Bed Catalyst Advantages

- **RG/PR catalysts are used by majors oil companies**
  - More than 200 references with promoted catalyst

- **Loading density adjusted to comply with customer needs**

- **The highest selectivity**
  - Fixed bed reforming catalysts are Pt / Re based therefore in order to change the yields we need to add something new
  - **Promoted catalyst**

- **The highest stability**
  - Pt sintering hindered with promoter
    - Longer cycles
    - Outstanding surface stability
    - Longer life

- **The highest chloride retention**
• Side reactions
  • Hydrocracking linked to very acidic sites
    • *Modified carrier*
  • Hydrogenolysis linked to metal activity
    • *Modified metals function*
• Promoter serves 2 roles
  • Lower $C_3$ & $C_4$ production
  • Lower $C_1$ & $C_2$ production

Higher hydrogen and $C_5^+$ yields
CCR Reforming
Catalysts
For 30 years the CCR catalyst market has been almost fully dominated by Pt/Sn
  • Any improvements maintaining the same formulation is very difficult

The market still wants higher yields
  • Mainly hydrogen
  • Mainly aromatics

Need for new catalyst formulation
The formulation needs
  - To be fully regenerable with standard equipment

The catalyst needs to keep at least the same
  - Chloride retention
  - Mechanical properties

Surface area stability needs to be improved to
  - Extend catalyst life
  - Ensure higher chloride retention throughout entire service life
  - Reduce production of fines
New Promoters developed to

1. Increase catalyst selectivity by minimizing the cracking reactions & ring opening
   - Higher $H_2$ & $C_{5+}$ yields

2. Increase catalyst stability by minimizing coke deposit on the catalyst
   - Allow to operate at lower recycle gas ratios
   - Yields increase
   - Reduction of utility consumption

3. As topping on the cake - the Pt content has been reduced while catalyst stability has increased
   - Lower cost
Today: 40 units in operation
Criterion Legacy & Axens CCR Catalyst in Non Axens Units
Axens design ; Non Axens design

Almost 100 units in Operation
# Axens CCR Reforming Catalyst Portfolio

<table>
<thead>
<tr>
<th></th>
<th>CR 600’s</th>
<th>AR 700’s</th>
<th>PS 40</th>
<th>PS 100</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Application</strong></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Gasoline</td>
<td></td>
<td>Aros</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasoline / Aromatics</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Pt, wt%</strong></td>
<td>0.25</td>
<td>0.30</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td><strong>Promoters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn + Others</td>
<td>(Multi-Promoted)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Moving bed density, t/m³</strong></td>
<td>0.65</td>
<td>0.65</td>
<td>0.54</td>
<td>0.54</td>
</tr>
<tr>
<td><strong>Main Attributes</strong></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Yields Strength</td>
<td>Activity Strength</td>
<td>Activity Strength</td>
<td>Activity Yields Strength</td>
<td></td>
</tr>
<tr>
<td><strong>Target Unit</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All</td>
<td>All</td>
<td>Competitor</td>
<td></td>
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<tr>
<td>High Density</td>
<td></td>
<td>Standard Density</td>
<td></td>
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CCR Reforming Standard Density Catalyst

**PS-40:** *Top performer for over 10 years!*
*Set the Standard for Performance Excellence.*

- **C₅⁺ yield:** 1.0 - 1.3 vol% more,
- **H₂ Yield:** 0.15 - 0.2 wt% more,
- **Feed Thru-put:** 15 - 30% more

- **Coke Lay-down:** 20–30% less,
- **Cl Consumption:** 10-30% less,
- **Make Up Catalyst:** 50-60% less

More than 40 Non-Axens Design Units Supplied Worldwide
PS-40 – Superior Surface Area Stability

Examples of Actual Surface Area Stability Curve of PS-40

- Catalyst surface area strongly influences catalyst life, activity & selectivity
Axens’ CR 600 & AR 700 provide the best surface area retention

- **Surface loss**
  - *Pt/Sn*
    - $\Delta$Surface = 55 m²/g
  - **CR 607**
    - $\Delta$Surface = 22 m²/g

Hydrothermal stability has been improved by a factor 2

- Operating conditions: Mixture of N₂ & H₂O
- 20% vol. water, at 650°C
Summary of Improvements New Generation Catalysts

- Better yields
  - Hydrogen + 0.1 wt%
  - Reformate + 1 wt%

- Coke make decreased by +30 %

- Fully regenerable with standard regenerator

- Surface area stability improved by a factor 2

- Lower platinum content

Targets are achieved
New Developments Standard Density Catalyst

• The result from the combination of Axens & Criterion’s catalytic Reforming technology. Leaders in catalytic formulations and superior Alumina Support Technology.

• Ultimate Selectivity.

• Improved Activity for units with no pinning limitations.

• Same Physical Characteristics as PS-40:
  • Lower Attrition Rates
  • Lower Fines make
  • Surface Area Retention
  • Chloride Retention

Available in 2012!
• Reasons to justify High Density Catalysts

• Activity constraints
  • Fire Heater limitations
    • High skin temperatures
    • High WAIT

• Pinning constraints
• Axens & Criterion Reforming business have merged

• The PR & PS Catalyst are still available

• New products are coming out soon

• R&D is working to take all the benefit of the two corporation knowledge
Thank You for your attention

Visit us at: http://www.axens.net