Axens State of the Art Solutions for Base Chemical Purification

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Axens’ State of the Art Solutions for Base Chemical Purification
Petrochemical & Polyolefins Market

Valuables
Monomers are available but comes with impurities

New technologies

Very performant catalysts
Very dependant of impurities presence

Purification systems
more sophisticate

Fulfill the market demands for very performing products
## Axens Product Offer for Monomers Purification

<table>
<thead>
<tr>
<th>Products</th>
<th>Type</th>
<th>Benefits</th>
</tr>
</thead>
<tbody>
<tr>
<td>AxSorb 537</td>
<td>3A Molecular Sieve (extrudates)</td>
<td>For drying: Excellent adsorption kinetics Very low olefin coadsorption Superior coking tolerance Good mechanical properties</td>
</tr>
<tr>
<td>AxSorb 913</td>
<td>13X Molecular Sieve</td>
<td>For Polar molecules removal &lt; 10Å diameter (Methanol, H2S, CO2, RSH, DMS, DMDS, Ketones, Nitriles, Ethers, olefins)</td>
</tr>
<tr>
<td>AxSorb 900/902</td>
<td>Hybrid (beads)</td>
<td>High performance polar molecules removal Low adsorption heat release Simplified operation</td>
</tr>
<tr>
<td>AxSorb 980/984</td>
<td>Promoted Alumina (beads)</td>
<td>For CO2 &amp; COS removal: Higher capacity products with high stability, lower coking No adsorption heat release</td>
</tr>
<tr>
<td>AxTrap 100 serie</td>
<td>Metal Oxide (beads)</td>
<td>High Arsine/Phosphine/S pickup capacity Loading/Unloading under air No pre/post-treatment</td>
</tr>
<tr>
<td>AxTrap 200 serie</td>
<td>(beads)</td>
<td>Mercury removal Loading/Unloading under air</td>
</tr>
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</table>
Axens Catalysts & Adsorbents Offer: Principles and Overview
Typical Impurities & Adsorbent Selection

- Depends on the specific impurities to be removed, the feedstock composition, the impurity and the outlet specifications:

  - Cracked-gas: \( \text{H}_2\text{O}, \text{NH}_3, \text{Hg} \)
  - Ethylene: \( \text{H}_2\text{O}, \text{O}_2, \text{CO}/\text{CO}_2, \text{H}_2\text{S}, \text{NH}_3, \text{NOx}, \text{N}_2, \) Alcohols (mainly methanol), Aldehydes, Ketones, Peroxides, Amines, Chlorides, Phosphine (PH\(_3\))
  - Propylene: \( \text{H}_2\text{O}, \text{O}_2, \text{CO}/\text{CO}_2, \) Sulfurs (\( \text{H}_2\text{S}, \text{Mercaptans}, \text{COS}, \text{DMDS} \)), \( \text{NH}_3, \) Alcohols (mainly methanol), Aldehydes, Ketones, Peroxides, Amines, Arsine (AsH\(_3\))

- Molecular Sieves (zeolites)
- Activated and Promoted Aluminas
- Hybrid or composite Material
- Metal Oxides

A large Adsorbents product range is needed
Catalyst - Selective Hydrogenation

- Target: Olefin Purification
- Reactions to promote:
  - Diolefins & Acetylenics Hydrogenation
  - Olefins Isomerization (if required)
- Other reactions are undesirable because:
  - Loss of desired products (ethylene and propylene)
  - Higher production of lower value products
  - Higher hydrogen consumption
  - Higher gums formation leading to reduce cycle

Specific catalyst is required depending on the application to be Selective
Base Chemical Purification: Ethylene
Typical Gas Phase Purification

From furnaces:
- AxSorb 533/537
- AxSorb 900/902
- AxSorb 980/984

Purification
- ppm
- ppb

Acetylene Converter
- LT 279
- LD 153

Impurities removed:
- H₂O
- NH₃
- Methanol
- CO₂
- H₂S
- RSH
- COS
- Arsine
- Phosphine

Polymer Grade Ethylene

AxSorb 533/537
AxSorb 900/902
AxSorb 980/984
AxTrap 191

Axens SOLUTIONS
C2 Front-end Hydrogenation Catalysts

- LT 279: Former Generation
  - Many references in vapor phase and more particularly in FE hydrogenation (excl. repeat orders and spare reactor)

- LD 153: New Generation
  - Differences between LD 153 and LT 279:
    - Higher selectivity to maximise ethylene yield ➔ multi promoted
    - Higher stability during CO fluctuations to avoid runaways
    - Low pressure drop ➔ 5mm beads
    - Improved resistance to contaminants (arsine, phosphine)
Base Chemical Purification: Propylene
Typical Liquid Phase Purification

- **Purification**
  - AxSorb 537
  - AxSorb 900/913
  - AxSorb 980/984
  - AxTrap 191 or 192/194

- **MAPD Converter**
  - ppm

- **C$_3$/C$_3$= Splitter**
  - LD 265
  - LD 273
  - LD 275

- Polymer Grade Propylene
- Product Propane

**Impurities removed**
- H$_2$O
- NH$_3$
- Methanol
- RSH/RSSR'
- COS
- Arsine
- Phosphine
- COS

AxSorb 900/913
AxSorb 980/984
AxTrap 191 or 192/194

Indian Petrochem 2019, 14-15 November, Mumbai
C₃ Cut: Catalyst Selection

- **Selectivity**: key to maximize profits
- LD 265 reference option: *many references* in C₃ hydrogenation
  - Standard design upstream PP Splitter, ideal for 1 stage scheme
- LD 273 high performance – bi-metallic noble metal *many references* in C₃ hydrogenation
- LD 275 new formulation: new catalyst for C₃ hydrogenation
  - Low Pd content ➔ Cost control
  - Propylene yield improvement ➔ 1% gain at 10 ppm MAPD
  - Industrial experience at 1 ppm MAPD
  - Long cycles > 3 years
Base Chemical Purification: Butene
**C₄ Cut: Catalysts for Butenes Maximization**

**H₂ make-up**

**C₄ feed**

**AxSorb 913**

**LD 265 or other LD**

**Product butadiene <10 ppm**

**Catalyst type depends on targeted butene isomer**

From ~50% butadiene down to ppm level → 2 stages scheme

Butadiene ~0.5 wt%

Many references to date
Butene-1: high value co-monomer for polyethylene
  ▶ Sustained growth (LLDPE and HDPE demand)

LD 271 catalyst for Butene-1 maximization
  ▶ High performance
    › Butadiene removal
    › High butene-1 yield
    › Low Pd content ➔ Cost control
    › Long operating cycles

C₄ Value Chain: Maximizing Butene-1
**C₄ Value Chain: Maximizing Butene-2**

- Butene-2: Intermediate for different applications
  - High purity isobutylene separation
  - Oligomerization, HF alkylation feedstocks
  - Propylene synthesis via metathesis, …
  - Butene-2 is the only reactive C4 isomer

**Hydroisomerization Optimal Solution**

Hydroisomerization towards butene-2:

The solution: LD 267 R or LD 269 catalyst
Base Chemical Purification: C5+
Pygas 1st Stage: Palladium or Nickel Catalyst

Pygas Value Chain (Typical)

- Pygas 1st Stage Hydrogenation (GHU-1)
- Pygas 2nd Stage Hydrogenation (GHU-2)
- Aromatics Production / Recovery

Main duty: Stabilize unstable diolefins & alkenyl aromatics
Prepare feed to Pygas 2nd Stage

Catalyst Type

<table>
<thead>
<tr>
<th>Targets</th>
<th>Palladium based catalyst</th>
<th>Nickel based catalyst</th>
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<tbody>
<tr>
<td>Feeds</td>
<td>Cost to fill</td>
<td>Maximum activity</td>
</tr>
<tr>
<td></td>
<td>LD 465</td>
<td>LD 485</td>
</tr>
<tr>
<td></td>
<td>Clean feed</td>
<td>Contaminated feed</td>
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Cost to fill

- LD 465
- LD 341
- LD 541 & LD 551
Pygas 2\textsuperscript{nd} Stage Dual Catalytic System

- **Neutral NiMo LD 145**
  - Many references
  - Neutral NiMo benchmark
  - Prevent gum formation in downstream HDT catalyst
  - Low ΔP feature (2-4 mm spherical)

- **HDT CoMo HR 606**
  - Many references
  - High activity
  - Aromatics selectivity
  - Evolution of former HR 306 & HR 406 many references
  - Multilobe extrudate

Main duty:
- Diolefins & styrenics saturation
- Olefins complete saturation, S removal

Feed: LD 145 → HR 606 1.6 → On-spec product: S, B.I.

Indian Petrochem 2019, 14-15 November, Mumbai
Conclusion

■ A complete and large Catalyst and Adsorbent portfolio: efficient and industrially proven

■ Deep Knowledge

■ New successful catalysts and adsorbents perfectly oriented towards petrochemicals market demand

■ Technical Services: Axens’ regional forces handle:
  ▶ follow-up
  ▶ troubleshooting (processes, catalysts and adsorbents)

A single source for multiple technologies & products to meet all olefins purification requirements
Thank you!

www.axens-solutions.net