BENZENE MANAGEMENT IN GASOLINE

XVIII FORO DE AVANCES DE LA INDUSTRIA DE LA REFINACIÓN
11 & 12 de Julio de 2012
Agenda

- Benzene Regulations
- Benzene Management Options
- Axens Benzene Saturation Technology
- Axens Commercial Experience
Benzene Regulations

- Benzene (B) is highly carcinogenic
- B < 1 vol. % limit in most developed countries
- US EPA MSAT II regulations:
  - Applicable to all gasoline (conventional and RFG)
  - As of Jan. 2011
    - Corporate average pool = 0.62 vol.% max B
    - Trade/credits arrangement possible
  - As of July 2012
    - Max refinery average B = 1.3 vol. % (no credits applicable)
- Gasoline benzene control envisioned in Mexico
Benzene Regulation

Benzene Management Options

Axens Benzene Saturation Technology

Axens Commercial Experience
### Benzene Pool Example

<table>
<thead>
<tr>
<th>Source</th>
<th>vol%</th>
<th>B, vol%</th>
<th>% Pool B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reformate</td>
<td>33</td>
<td>4.8</td>
<td>84.2</td>
</tr>
<tr>
<td>FCC Gasoline</td>
<td>38</td>
<td>0.7</td>
<td>14.1</td>
</tr>
<tr>
<td>Other</td>
<td>29</td>
<td>0.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Pool</td>
<td>100</td>
<td>1.9</td>
<td>100</td>
</tr>
</tbody>
</table>

**Reformate is The dominant B contributor**

![Bar chart showing benzene levels for different sources](chart.png)

- **Reformate Benzene Control (85% reduction)**
  - Reformate: 0.52% (14% of the pool)
  - Others: 46% (3% of the pool)
  - FCC N: 51% (51% of the pool)

**New Limit**
Native Benzene

Benzene produced in Reformer
  - Precursors (MCP, CH, C₆’s)
  - Hydrodealkylation reactions
1. Pre-treatment of reformer feed
   - Fractionation of Benzene precursors
   - Isomerization

2. Changes to Reformer Operation
   - Catalyst change out
   - Revamp to lower pressure
3. Post-treatment of reformate

- Extraction
- Saturation
- Isomerization
- Benzene Alkylation
Least Expensive But Least Flexible Method

- Typically 50% B decrease by removal of B precursors (MCH, CH, B)
- Existing splitters are typically overloaded
  - sloppy cut
- Impact on isomerization unit
  - increase B exotherm & C7+ cracking
  - isomerization inhibitor
- Octane loss may be compensated by octane boosters (oxygenates, alkylate)
  - not by reformer severity increase
Octane Improvement

- Ethanol Mandate through RFS provides additional octane
- Refiners may be octane long

RVP increase

- Ethanol Mandate through RFS increases RVP
- Isomerization units create additional pressure on RVP constraint
Reformer Operation Changes

Lowering Reformer Pressure

- Increased hydrogen production
- Increased gasoline yield and lower product RVP
- HDA reactions decreased (lower Benzene make)
- Impact on recycle compressor and cycle length
Processing options

- Octanizing (CCR)
- Dualforming

Catalyst Change out

- Catalyst with lower B make have been commercially demonstrated by Axens
Impact of Pressure & Cut Point

Benzene Yield ex Reformer - Prefractionation Impact

Benzene yield, wt% / Feed

- Increasing RON

Typical

Prefrac

MP CCR

SR

MP CCR

LP CCR

Semi-Reg

Axens
Benzene Extraction

- Case specific – aromatics business
- Gasoline yield decrease

Benzene Alkylation

- No H₂ consumption
- Competes with Alkylation and Petrochemicals for propylene use
- Limited B conversion
- Very limited commercial experience
Benzene Saturation

- Least expensive post-treat solution
- Gasoline yield increased (~ +20%)
- Impact on pool octane to be assessed on a case by case basis
  - Possibility to isomerize the light reformate

- Highest flexibility
  - Reformer feed quality & operation severity
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Benzene Saturation Principles

- Separation Toluene / Benzene
  - Reformate Splitter
    - Minimize octane loss
    - Minimize $H_2$ consumption
- Benzene hydrogenated into cyclohexane
- Olefins (if any) hydrogenated to corresponding Paraffins
Axens’ Benfree™ Solutions

Option 1
Conventional Benfree$_c$

Option 2
Reactive Dist Benfree$_{RD}$

Axens is in a unique position to provide the best scheme for each application.
Conventional Benzene Saturation: Benfree\textsubscript{C}

- Fuel Gas
- Stabilizer
- Light Reformate
- Recycle
- H\textsubscript{2}
- Reactor
- HP Purge
- Fuel Gas

Reformate Splitter

Light Ref.

H\textsubscript{2}

Reactor

HP Purge

Stabilizer

Recycle

Light Reformed

Heavy Reformate

Benfree\textsubscript{C}
Benfree<sub>C</sub> Highlights

- **Good Benzene / Toluene Separation**
  - Minimize Toluene carry-over overhead

- **Maximum Benzene Conversion**
  - Product B < 0.1 %

- **Low Operating Pressure**

- **No cracking Reactions**
Reactive Distillation Benfree: Benfree$_{RD}$

Reformate

Splitter

Reformate

H$_2$

Light Ends

Isomerization

C$_5$-C$_6$

Low Benzene Reformate to Gasoline Pool
Lower equipment count
- No feed pump
- No separator drum
- No stabilizer and associated equipment
- Minimum footprint

Distillation/reaction config. advantages
- Limits C$_7$’s and Naphthenes in Light Ref.
  - *No benzene-C$_7$ azeotrope* $\rightarrow$ *lower LPG make in isom. unit*
  - *Limited Cyclohexane* $\rightarrow$ *no isom. catalyst inhibition*
Benfree$_{RD}$ Highlights (2/2)

- Separation of Reactor and Distillation
  - Conventional distillation technology
  - Better control of each section
  - Better optimization
    - Control of benzene at reactor inlet (on-line analyzer)

- No $\text{H}_2$ recycle compressor or blower

- No cracking Reactions

- Benfree™ catalyst located outside the splitter
  - Catalyst change-out without splitter S/D
  - Production of low benzene heavy reformate at all times
• Benzene Conversion Requirement:
  – Below 90% $\rightarrow$ Benfree$_{RD}$
  – Above 95% $\rightarrow$ Benfree$_{C}$
  – Between 90% - 95% $\rightarrow$ Case Specific
# Scheme Comparison at 85 - 90% B Conversion

<table>
<thead>
<tr>
<th>Comparison</th>
<th>Benfree&lt;sub&gt;C&lt;/sub&gt;</th>
<th>Benfree&lt;sub&gt;RD&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment Count</td>
<td>Base</td>
<td>Base – 35%</td>
</tr>
<tr>
<td>Capital Cost</td>
<td>Base</td>
<td>Base – 30%</td>
</tr>
<tr>
<td>Utilities Cost</td>
<td>Base</td>
<td>Base</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt; &amp; Octane Cost</td>
<td>Base</td>
<td>Base</td>
</tr>
<tr>
<td>Plot area</td>
<td>Base</td>
<td>Base – 35%</td>
</tr>
</tbody>
</table>
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## Commercial Experience

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>$\text{Benfree}_C$</th>
<th>$\text{Benfree}_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Awards</td>
<td>51</td>
<td>40</td>
<td>11</td>
</tr>
<tr>
<td>Operating</td>
<td>37</td>
<td>31</td>
<td>6</td>
</tr>
<tr>
<td>Ni / Pt</td>
<td>(32/19)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In general, Pt based catalyst upstream of isomerization unit. Ni based catalyst for stand-alone unit.
Feed & Product Benzene

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Feed & Product Benzene
- Start Up: 1999
- Cycle length: 10 + years with same catalyst load
- Typical Feed B: 15 v% (in Light Ref.)
- Typical Product B: 0.1 v%
Start Up: January 2000

Typical Feed B : 4.0 v% (Full Range Ref.)

Typical Product B: 0.6 v% (85 % Conv.)

Catalyst:
- 1st Catalyst change-out May 2008 (> 8 years)

Reliability: close to 100%
Benzene regulations

- No pay-out for investment (stay in business)
- Seek lowest capital cost solution

Different routes available

- Pre-fractionation route often insufficient
- Post-fractionation offers the most flexibility
  - Benzene saturation most selected option

Axens offers commercially proven B saturation processes & catalysts

- Benfree$_c$, Benfree$_{RD}$
- Ni catalyst system, Pt catalyst system

Managing benzene in the gasoline pool requires a broad perspective on all sources & controls:

- Reformer, isomerization, FCC gasoline, ethers, …
- Axens provides expertise in all of these areas
Q & A

Thank you for your attention!

Visit our new website: www.axens.net