Refining/Petrochemical Integration – A New Paradigm
Anil Khatri, GTC Technology
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Present integration schemes focus on propylene, and miss the potential to capture added value from aromatics.

Valuable components exist in FCC gasoline – heavy olefins & aromatics.

Patented GTC purification and conversion technology can upgrade traditional fuel components to high value petrochemicals.

### Presentation Themes

<table>
<thead>
<tr>
<th>Component</th>
<th>Value Relative to Unleaded Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>0.87</td>
</tr>
<tr>
<td>Unleaded Gasoline</td>
<td>1.00</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.13</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.15</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1.24</td>
</tr>
<tr>
<td>Mixed Xylenes</td>
<td>1.26</td>
</tr>
<tr>
<td>Paraxylene</td>
<td>1.43</td>
</tr>
<tr>
<td>Propylene</td>
<td>1.55</td>
</tr>
<tr>
<td>Styrene</td>
<td>1.63</td>
</tr>
</tbody>
</table>

Benzene  
Toluene  
Mixed Xylenes  
Propylene
Presentation Overview

➢ Gasoline demand and clean fuel regulations around the world

➢ Process for recovering aromatics from FCC Gasoline - GT-BTX-PluS®

➢ Processes for utilization of FCC olefins

➢ Case study – No gasoline, only p-xylene and benzene
## World Gasoline Demand – Stagnant or Decreasing

### Major Regions Gasoline Supply/Demand

<table>
<thead>
<tr>
<th></th>
<th>Unit: 1,000 B/D</th>
<th>2006</th>
<th>2008</th>
<th>2010</th>
<th>2012*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>US</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasoline Demand</td>
<td></td>
<td>10,929</td>
<td>11,120</td>
<td>11,340</td>
<td>10,850</td>
</tr>
<tr>
<td>Gasoline Surplus (Deficit)</td>
<td></td>
<td>(1,135)</td>
<td>(1,100)</td>
<td>(870)</td>
<td>(200)</td>
</tr>
<tr>
<td><strong>EUROPE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasoline Demand</td>
<td></td>
<td>2,546</td>
<td>2,430</td>
<td>2,334</td>
<td>2,250</td>
</tr>
<tr>
<td>Gasoline Surplus (Deficit)</td>
<td></td>
<td>902</td>
<td>1,000</td>
<td>1,200</td>
<td>1,150</td>
</tr>
<tr>
<td><strong>MIDEAST GULF</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasoline Demand</td>
<td></td>
<td>1,193</td>
<td>1,368</td>
<td>1,545</td>
<td>1,750</td>
</tr>
<tr>
<td>Gasoline Surplus (Deficit)</td>
<td></td>
<td>(250)</td>
<td>(120)</td>
<td>(200)</td>
<td>(300)</td>
</tr>
<tr>
<td><strong>ASIA PACIFIC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasoline Demand</td>
<td></td>
<td>3,966</td>
<td>4,210</td>
<td>4,505</td>
<td>4,800</td>
</tr>
<tr>
<td>Gasoline Surplus (Deficit)</td>
<td></td>
<td>150</td>
<td>250</td>
<td>300</td>
<td>200</td>
</tr>
</tbody>
</table>

Source: Asian Pacific Energy Consulting

* Estimated
## Gasoline Specification

### Limitation Imposed on Aromatics

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur, ppm, max</td>
<td>1,000/500</td>
<td>150</td>
<td>50 (10)</td>
<td>10</td>
</tr>
<tr>
<td><strong>Aromatics, vol%, max</strong></td>
<td>-</td>
<td>42</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Olefins, vol%, max</td>
<td>-</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td><strong>Benzene, vol%, max</strong></td>
<td>5.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Aromatics Trends

Aromatics demand for petrochemicals is growing

MIXED XYLENES DEMAND BY REGION
(Million Tons)

Sources: CMAI
FCC Gasoline Desulfurization

Conventional Three-Stage Process

- FCC Naphtha
  - MCN (70-150°C)
  - LCN
  - C5-iC6-
  - Optional Caustic Extraction
  - Medium HDS
  - Mild HDS
- HCN (150°C-EP)
  - Severe HDS
- ULS Gasoline Blending

- C₆-C₉ Olefins
  - Saturation (unavoidable)
- Sulfur
  - Desulfurization (needed)
Aromatics Extraction with GT-BTX PluS®

- FCC Naphtha
- LCN
- C₅₋iC₆⁻
- (optional) Mild HDS
- Raffinate: Paraffins + Olefins
- Extract: Sulfur + Aromatics
- H₂ H₂S
- HCN
- 150°C-EP
- Severe HDS
- ULS Gasoline Blending
- Gasoline Blending
- GT-BTX PluS®
- MCN
- 70-150°C
- HDS
- Aromatics
- Caustic Extraction
- ULS
Liquid-liquid Extraction

Extractive Distillation

H₂O

Raffinate

Extract

Feed

Raffinate

Extract

Solvent

Solvent
## Different Solvent Systems for Aromatics Recovery

<table>
<thead>
<tr>
<th>Solvent</th>
<th>S/F</th>
<th>Relative volatility (α) n-C$_7$/benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Techtiv (GT-BTX®)</td>
<td>3.0</td>
<td>2.44</td>
</tr>
<tr>
<td>Sulfolane</td>
<td>3.0</td>
<td>2.00</td>
</tr>
<tr>
<td>N-methyl pyrrolidone</td>
<td>3.0</td>
<td>1.95</td>
</tr>
<tr>
<td>N-formyl morpholine</td>
<td>3.0</td>
<td>1.89</td>
</tr>
<tr>
<td>Tri-ethylene glycol</td>
<td>3.0</td>
<td>1.44</td>
</tr>
<tr>
<td>Tetra-ethylene glycol</td>
<td>3.0</td>
<td>1.39</td>
</tr>
<tr>
<td>Glycol blends (CAROM)</td>
<td>3.0</td>
<td>1.35</td>
</tr>
<tr>
<td>No solvent</td>
<td>0</td>
<td>0.57</td>
</tr>
</tbody>
</table>

(α) R.V. = ($y_A/x_A$)/($y_B/x_B$)
Typical Refinery Configuration with GT-BTX PluS® - Products to Gasoline

- Zero Δ in octane value
- Low benzene
- Low sulfur
Typical Refinery Integrated with Aromatics using GT-BTX PluS®

Much preferred to recycling FCC naphtha to catalytic reforming
Options for FCC C$_4^+$ Olefins

- Gasoline blending $\rightarrow$ zero change in octane value
desulfurized
debenzenized

- Aromatization $\rightarrow$ BTX, PX

- Re-cracking $\rightarrow$ C3$^=$
Aromatization: Generate BTX from Low Value Streams

- FCC C4/C5
- FCC C6 – C8, non-aromatic cut
- Steam Cracker heavy olefins
- Dry Gas
- LPG
- Aromatics
Additional Aromatics from FCC C₄ – C₈ Olefin Fraction

More Aromatics from Non-Traditional Feedstock
Refinery configuration with GT-BTX PluS® to facilitate increased Propylene

Extends Range of FCC Naphtha Recycle
• Technically advanced extraction process enables

  ➢ Desulfurized gasoline to < 15 ppm sulfur with zero octane loss
  ➢ Reduced benzene in cracked gasoline to < 0.5% benzene
  ➢ FCC olefins preserved for conversion to aromatics or propylene

Patented process – available through GTC Technology
*Stream is sent to Aromatics Complex for Benzene and Paraxylene recovery*
### Incremental Aromatics from Gasoline Source

<table>
<thead>
<tr>
<th>C&lt;sub&gt;6&lt;/sub&gt;-C&lt;sub&gt;9&lt;/sub&gt; AROMATICS</th>
<th>KG/HR</th>
<th>TPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>INDIGENOUS FCC</td>
<td>11,427</td>
<td>97,126</td>
</tr>
<tr>
<td>PYGAS</td>
<td>8,029</td>
<td>68,245</td>
</tr>
<tr>
<td>AROMATIZATION</td>
<td>26,525</td>
<td>225,471</td>
</tr>
<tr>
<td>TOTAL</td>
<td>45,981</td>
<td>390,842</td>
</tr>
</tbody>
</table>

Total incremental BTX = 320 KTA
Conclusions

- Refinery/Petrochemical integration involves more than simple propylene recovery
- Recycling FCC gasoline to naphtha reforming is not true integration, and misses the main point of process efficiency
- GT-BTX PluS® is the enabling technology which permits the best use of molecules to their highest value