New Feedstocks and Advances in Technologies to Produce Paraxylene

GTC Technology Day

16 April • Hotel Le Meridien • New Delhi
Aromatics Generation

Hydrotreated Naphtha

Catalytic Reformer

Splitter

C9/C10

Transalkylation

Aromatics Extraction

Benzene Column

C5

C5 – C7 Raffinate

Toluene Product

Paraxylene Recovery

Xylene Isomerization

Benzene Product

Toluene Column

Paraxylene

Deheptanizer

C9 / C10

Xylene Column

Heavy Aromatics Column

C11 +

Aromatics Generation
Maximizing PX Production in a Modern Refinery
– Sourcing New Feedstocks

• A modern refinery *is or is going to be* a Refinery – Petrochemical Integrated Complex

• Sourcing new feedstocks for PX Production
  - Pyrolysis Gasoline
  - FCC Naphtha
  - C4/C5 streams
  - Methanol
Pyrolysis Gasoline from Crackers

1 MMTPA Ethylene producing cracker
- Pygas stream with potential to produce up to 100 KTA additional PX

<table>
<thead>
<tr>
<th>Component (mol%)</th>
<th>Raw Pygas Liquid</th>
<th>C7-C8 Cut Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>30.57</td>
<td>0.04</td>
</tr>
<tr>
<td>Toluene</td>
<td>20.80</td>
<td>69.07</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>1.14</td>
<td>13.37</td>
</tr>
<tr>
<td>Xylene</td>
<td>2.69</td>
<td>8.97</td>
</tr>
<tr>
<td>Styrene</td>
<td>2.86</td>
<td></td>
</tr>
<tr>
<td>C9 Hydrocarbons</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C10 - 204 C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Pyrolysis Gasoline from Crackers

Typical Processing of Pygas

1st Stage

Raw Pygas

$H_2$

Off Gas

$C_5$

2nd Stage

$C_6-C_8$ Stream

$H_2$

$C_6-C_8$ Raffinate

GT-BTX Unit

Benzene Product

C7-C8 Product to gasoline blending
Pyrolysis Gasoline from Crackers

Processing of Pygas in a Refinery – Petrochemical Integrated Complex

1st Stage

Raw Pygas → Off Gas

H₂ → C₅

2nd Stage

H₂ → C₆-C₈ Stream

C₆-C₈ Stream → GT-BTX Unit

Benzene Product
Toluene to TA/TM
MX for PX Recovery

C₆-C₈ Raffinate

C₅

C₆+ Product

- GTC is the leading technology provider for full-range BTX extraction
Typical FCC Naphtha Processing for Gasoline Production

- FCC Naphtha
- Selective Hydrogenation Unit
- LCN C5-iC6
- MCN 70-170°C
- Severe HDS
- Hydrogen
- HCN
- To NHT/Reformer
- ULS Gasoline

Hydrotreating and reforming FCC naphtha destroys the valuable olefins
## FCC Naphtha

### Carbon Number Distribution and PONA Typical High Severity FCC Naphtha

<table>
<thead>
<tr>
<th>C number</th>
<th>n-Paraffin</th>
<th>iso-Paraffin</th>
<th>Olefin</th>
<th>Naphthene</th>
<th>Aromatics</th>
<th>Total</th>
<th>vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4</td>
<td>0.11</td>
<td>0.00</td>
<td>1.52</td>
<td>0.00</td>
<td>0.00</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>C5</td>
<td>1.60</td>
<td>11.54</td>
<td>20.36</td>
<td>0.31</td>
<td>0.00</td>
<td>33.81</td>
<td></td>
</tr>
<tr>
<td>subtotal</td>
<td>1.71</td>
<td>11.54</td>
<td>21.88</td>
<td>0.31</td>
<td>0.00</td>
<td>35.44</td>
<td></td>
</tr>
<tr>
<td>C6</td>
<td>0.75</td>
<td>4.37</td>
<td>5.88</td>
<td>1.50</td>
<td>4.24</td>
<td>16.74</td>
<td></td>
</tr>
<tr>
<td>C7</td>
<td>0.68</td>
<td>1.69</td>
<td>2.46</td>
<td>1.72</td>
<td>11.02</td>
<td>17.57</td>
<td></td>
</tr>
<tr>
<td>C8</td>
<td>0.36</td>
<td>1.34</td>
<td>0.98</td>
<td>1.04</td>
<td>12.30</td>
<td>16.02</td>
<td></td>
</tr>
<tr>
<td>C9</td>
<td>0.14</td>
<td>0.67</td>
<td>0.06</td>
<td>0.29</td>
<td>8.58</td>
<td>9.74</td>
<td></td>
</tr>
<tr>
<td>subtotal</td>
<td>1.93</td>
<td>8.07</td>
<td>9.38</td>
<td>4.55</td>
<td>36.14</td>
<td>60.07</td>
<td></td>
</tr>
<tr>
<td>C10</td>
<td>0.11</td>
<td>0.33</td>
<td>0.01</td>
<td>0.00</td>
<td>3.35</td>
<td>3.80</td>
<td></td>
</tr>
<tr>
<td>C11</td>
<td>0.09</td>
<td>0.19</td>
<td>0.00</td>
<td>0.00</td>
<td>0.32</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>C12</td>
<td>0.00</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.15</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>subtotal</td>
<td>0.20</td>
<td>0.57</td>
<td>0.00</td>
<td>0.00</td>
<td>3.82</td>
<td>4.59</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>3.84</td>
<td>20.18</td>
<td>31.26</td>
<td>4.86</td>
<td>39.96</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>
## Gasoline and Aromatics Component Value

<table>
<thead>
<tr>
<th>Components</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>Mixed Xylenes</td>
<td>1.26</td>
</tr>
<tr>
<td>Paraxyline</td>
<td>1.43</td>
</tr>
<tr>
<td>Styrene</td>
<td>1.63</td>
</tr>
</tbody>
</table>
Introducing GT-BTX PluS®: Segregating Aromatics

FCC Naphtha → SHU → LCN (C5-70°C) → ULS Gasoline

FCC Naphtha → SHU → MCN (70-170°C) → GT-BTX PluS® → ULS Gasoline or Petrochemical Production

FCC Naphtha → SHU → HCN (170°C - EP) → HDS → Desulfurized Olefin-rich Raffinate → Aromatics for PX Production

Aromatics for PX Production

ULS Gasoline
Aromatics Recovery from FCC Gasoline

Optimized Three-Stage Process


Extract: Sulfur + Aromatics → GT-BTX PluS® → Aromatics

LCN C5-iC6 → ULS Gasoline
Refinery Configuration with GT-BTX PluS® to facilitate increased Propylene
Typical Refinery Integrated with Aromatics using GT-BTX PluS®

Crude Oil → Crude Distillation → Wide Naphtha Range

- FCCU
- Desulfurization
- Naphtha Reforming
- Hydrotreating

Gasoline → Isomerization → Aromatics Plant

- GT-Aromatization
- Olefinic Raffinate

Fuel → GT-BTX PluS

ULS Gasoline

Kerosene → Gasoil

- Fuel
- Olefinic Raffinate

Benzene
Toluene
Xylenes
Heavy Aromatics
C4/C5 Streams - Aromatization

Typical Feed and Product

**Typical Feeds**
- Olefinic hydrocarbon streams
  - Mono-olefin C4 or C5 fractions
  - Olefinic C6-C8 fractions from partially hydrotreated pygas
  - FCC C4/C5

**Typical Products**
- C6-C9 aromatics
C4/C5 Streams - Aromatization

- Nano-scaled zeolite with metal
- High activity and Aromatics selectivity
- No Hydrogen
- Low pressure, moderate temperature
**C4/C5 Streams - Aromatization**

**Feed 1**

<table>
<thead>
<tr>
<th>Items</th>
<th>Content /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3</td>
<td>0.5</td>
</tr>
<tr>
<td>i-C4</td>
<td>45.3</td>
</tr>
<tr>
<td>N-C4</td>
<td>14.0</td>
</tr>
<tr>
<td>C4=</td>
<td>39.8</td>
</tr>
<tr>
<td>C5</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Products 1**

<table>
<thead>
<tr>
<th>Items</th>
<th>Content /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>3.3</td>
</tr>
<tr>
<td>Dry Gas</td>
<td>15.8</td>
</tr>
<tr>
<td>LPG</td>
<td>25.8</td>
</tr>
<tr>
<td>Liquid</td>
<td>53.6</td>
</tr>
</tbody>
</table>

**Feed 2**

<table>
<thead>
<tr>
<th>Items</th>
<th>Reforming Topped Oil</th>
<th>Raffinate Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>C5</td>
<td>75.5</td>
<td>11.9</td>
</tr>
<tr>
<td>C6</td>
<td>22.8</td>
<td>51.4</td>
</tr>
<tr>
<td>C7</td>
<td>1.7</td>
<td>25.4</td>
</tr>
<tr>
<td>C8</td>
<td>0.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Products 2**

<table>
<thead>
<tr>
<th>Feed</th>
<th>Reforming Topped Oil</th>
<th>Raffinate Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield /%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry Gas</td>
<td>22.69</td>
<td>21.13</td>
</tr>
<tr>
<td>LPG</td>
<td>23.19</td>
<td>24.62</td>
</tr>
<tr>
<td>Liquid</td>
<td>54.12</td>
<td>54.24</td>
</tr>
</tbody>
</table>

**Liquid Product:**
- Benzene: 21%
- Toluene: 44%
- Xylenes: 26%
- A9: 9%

**Large Potential for PX production**
Methanol – Toluene Methylation

Toluene based PX technology to produce mixed xylenes

- Toluene disproportionation (TDP)
  \[ 2 \text{C}_8 \text{H}_8 \rightleftharpoons \text{C}_6 \text{H}_6 + \text{C}_7 \text{H}_8 \]

- Toluene transalkylation (TA) with C9+
  \[ \text{C}_8 \text{H}_8 + \text{C}_9 \text{H}_{12} \rightleftharpoons \text{C}_7 \text{H}_8 + \text{C}_{10} \text{H}_{14} \]

- Selective toluene disproportionation (STDP) to produce PX-rich xylenes (PX 80-93%)
  \[ 2 \text{C}_8 \text{H}_8 \rightleftharpoons \text{C}_7 \text{H}_8 + \text{C}_9 \text{H}_{12} \]

By-product benzene is inevitable due to imbalance of methyl group
Limitation for PX from Reformate – Methyl Group

To maximize PX, aromatics from reformate has a shortage of methyl groups

<table>
<thead>
<tr>
<th></th>
<th>Typical in Reformate (wt%)</th>
<th>To PX</th>
<th>Methyl Group Shortage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>10</td>
<td>Two methyl group addition</td>
<td>2</td>
</tr>
<tr>
<td>Toluene</td>
<td>29</td>
<td>One methyl group addition</td>
<td>1</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>6</td>
<td>Ethyl group converting into two methyl group</td>
<td>0, 2</td>
</tr>
<tr>
<td>Mixed xylenes</td>
<td>28</td>
<td>Purification and isomerization</td>
<td>0</td>
</tr>
<tr>
<td>C9+ Aromatics</td>
<td>12</td>
<td>C2+ alkyl group removal and methyl group transalkylation</td>
<td>~0</td>
</tr>
</tbody>
</table>
NaphthConcept of Toluene Methylation
– Addition of Methyl Group to Aromatic Rings Processing Technology by GTC

Toluene + Methanol ⇌ Xylenes + Water

Aromatics (reformate, FCC, etc.) → Maximized PX

Methyl group

Methanol

* Methyl groups can be added to Benzene also
**Toluene Methylation Favors Xylenes**

- Maximum PX production on same toluene basis
- Eliminates benzene production
- Methanol from coal, natural gas or biomass makes it attractive as a secondary feedstock
GT-TolAlk℠ Process Scheme

Simple, fixed-bed design with no hydrogen compressor or circulation
GT-TolAlk® – Xylenes Potential

- 80% methyl group from methanol is in xylenes and trimethylbenzene
- EB in xylenes is ~ 0.1 wt%

<table>
<thead>
<tr>
<th>Reactant</th>
<th>KTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>400</td>
</tr>
<tr>
<td>MeOH</td>
<td>189</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Products</th>
<th>KTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed Xylenes</td>
<td>390</td>
</tr>
<tr>
<td>C9/C10*</td>
<td>80</td>
</tr>
<tr>
<td>Fuel</td>
<td>14</td>
</tr>
</tbody>
</table>

* To Transalkylation
Maximized Paraxylene Production

Utilization of available and cheaper feedstocks to maximize PX production on same crude oil basis

Hydrotreated Naphtha

Catalytic Reformer

Hydrotreated Pygas

GT-Aromatization℠

GT-BTX PluS®

FCC Naphtha

Additional Paraxylene

Deheptanizer

Xylene Isomerization

Paraxylene Recovery

Benzene Column

Aromatics Extraction

C9/C10

Transalkylation

C5, C5 – C7 Raffinate

MeOH

GT-TolAlk℠
Conclusion

• Utilization of all available feed streams in refinery and new cheaper feedstock can maximize para-xylene production on same crude oil basis
• The available streams in refinery are pygas, FCC naphtha and C4/C5 light hydrocarbons
• Methanol, a cheaper feedstock coming from coal and natural gas, can increase PX production potential
• GTC’s commercially proven processes can help refiners upgrade these feeds to high value PX product
  • Full Range B,T,X extraction from Pygas stream using GT-BTX®
  • TX extraction of FCC naphtha using GT-BTX PluS®
  • C4/C5 light HC Aromatization using GT-Aromatization℠
  • Toluene Methylation using GT-TolAlk℠
• These technologies along with GTC’s CrystPX℠, GT-TransAlk℠ and GT-IsomPX℠ can provide optimized PX production complex to refiners
• GTC’s innovative applications of Dividing Wall Columns provides further operational benefits in PX complex
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