Aromatics and Sulfur Extraction from FCC Gasoline

Sachin Joshi, Director/Licensing – Middle East & India
Gary Martin, Manager/Business Development – Refining Technologies
Part 1

1. FCC Gasoline Desulfurization without losing Octane

2. Recovering Aromatics from FCC Gasoline
FCC Gasoline – Olefins/Sulfur/RON Distribution

Olefin Distribution

<table>
<thead>
<tr>
<th>C_5</th>
<th>C_6</th>
<th>C_7</th>
<th>C_8</th>
<th>C_9</th>
<th>C_10</th>
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<tbody>
<tr>
<td>LCN</td>
<td>MCN</td>
<td>HCN</td>
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Thiophenic Sulfur

<table>
<thead>
<tr>
<th>C_5</th>
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<table>
<thead>
<tr>
<th>Olefin</th>
<th>Thiophenic Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCN</td>
<td>High</td>
</tr>
<tr>
<td>HCN</td>
<td>Low</td>
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</table>

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FCC Gasoline – Olefins/Sulfur/RON Distribution

Olefin Distribution

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<tr>
<th>C5</th>
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<tr>
<td>LCN</td>
<td>High</td>
</tr>
<tr>
<td>HCN</td>
<td>Low</td>
</tr>
<tr>
<td>MCN</td>
<td>Medium</td>
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</table>

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FCC Gasoline Desulfurization

Typical Gasoline Desulfurization Process

New regulations require sulfur reduction > 99%.

Figure 3 – Dependence of the loss of octane number on the level of hydrodesulfurization in HDS section of Prime G based on data by Axens
Olefin Saturation is the Problem

<table>
<thead>
<tr>
<th></th>
<th>RON</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C - C - C - C - C = C ) (Hexene)</td>
<td>74-94</td>
</tr>
<tr>
<td>( C - C - C - C - C - C ) (Hexane)</td>
<td>24</td>
</tr>
</tbody>
</table>
GT-BTX PluS® Gasoline Treating

Gasoline Desulfurization Process with GT-BTX PluS®

- FCC Naphtha
- Hydrogen
- SHU

- MCN 158-300°F
- LCN
- C5-iC6

- HCN 300°F - EP

- Severe HDS

- Aromatics/ Sulfur-rich Extract
- Less Hydrogen
- Benzene cut-off (optional)

- Desulfurized Olefin-rich NA Raffinate

- GT-BTX PluS®

- ULS Gasoline

Majority Olefins Taken away from HDS, minimizing octane loss from saturation

Significantly lowers octane loss

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GT-BTX PluS® - General Flow Scheme

Hydrocarbon Feed
Lean Solvent
Extractive Distillation Column (EDC)
Aromatics Rich Solvent
Raffinate

Olefins Diverted from HDS

Solvent Recovery Column (SRC)

Very Low Olefins Minimize Olefin Saturation and Octane Loss in HDS

Techtiv® DS

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Key Benefits of GT-BTX PluS®

- Reduction of octane loss
- Eliminates the need for increasing reformer severity
- Doubles time between shutdowns for semi-regen reformers
- H2 consumption across HDS block reduced
- HDS flow rate reduced
- Provides for ability increase reformer severity in future for octane needs of high compression engines
- Option of producing diesel from the bottom of naphtha splitter
GT-BTX PluS® - Case Study #1
GT-BTX PluS® Operation – Case Study #1

• GT-BTX PluS® Unit started up in 1Q 2016.
• GT-BTX PluS® unit was added to an existing FCC gasoline HDS unit.
• Project duration from contract signing to performance test: less than a year
GT-BTX PluS® - Case Study

Refiner configuration before implementing GT-BTX PluS®

- FCC Gasoline to SHU
- Hydrogen to SHU
- Light Column
- MCN/HCN
- HDS
- Off-gas
- Hydrotreated Gasoline
- Treated FCC gasoline to gasoline blending

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GT-BTX PluS® Process Configuration

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GT-BTX PluS® Operating Reference

MCN/HCN Splitter
SRC
EDC

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FCC Gasoline Desulfurization Unit Performance post-GT-BTX PluS®

• Total liquid yield: 99.6%+
• Total sulfur removal rate: 99%+
• H2 unit consumption: Reduced by 60%
• Cost of production: unchanged (steam consumption increased but H2 reduced)
• Octane improvement: RON increase of 3.5
# Sulfur Balance

<table>
<thead>
<tr>
<th>Stream</th>
<th>Sulfur wppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full-range FCC gasoline feed</td>
<td>498 – 660</td>
</tr>
<tr>
<td>Light gasoline</td>
<td>11 – 15</td>
</tr>
<tr>
<td>GT-BTX PluS raffinate</td>
<td>4 – 5</td>
</tr>
<tr>
<td>Product from HDS</td>
<td>2 – 4</td>
</tr>
<tr>
<td>Full-range desulfurized FCC gasoline product</td>
<td>2 – 7</td>
</tr>
</tbody>
</table>
GT-BTX PluS® Operation – Case Study #2

• GT-BTX PluS® Unit started up in 3Q 2016
• GT-BTX PluS® unit was added to an existing FCC gasoline HDS unit.
• Project duration from contract signing to performance test: 14 months
• Prior to the revamp the unit was losing 3.4 RON
GT-BTX PluS® - Case Study #2

Gasoline Desulfurization Process with GT-BTX PluS®

FCC Naphtha

SHU

S = 456ppm
RON = 92.5

Hydrogen

S = 0.07%

MCN

GT-BTX PluS®

Extract

S = 0.143%

Sulfur

S = 12ppm

ULS Gasoline

S = 13.2ppm

Olefin-rich NA Raffinate

S = 9.1ppm
RON = 91.9

S = 4.4ppm

Severe HDS

S = 9ppm
RON = 92.5

S = 0.07%

Hydrogen

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GT-BTX PluS® Operating Reference

Tomorrow’s Innovation Today • Sept. 24, 2018 • Houston
FCC Gasoline Desulfurization Unit Performance post-GT-BTX PluS®

• Total liquid yield: 99.5%+
• Total sulfur removal rate: 99%+
• H2 unit consumption: Reduced by 65%
• Octane improvement: RON loss reduced from 3.4 to 0.6
Part 2

1. FCC Gasoline Desulfurization without losing Octane

2. Recovering Aromatics from FCC Gasoline
GTC Portfolio in Refining, Petrochemical & Polyester Industry
Generating Aromatics from FCC Gasoline

GTC Portfolio in Refining, Petrochemical & Polyester Industry

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FCC Naphtha: Prevalent Practice

Hydrotreating destroys olefins, Benzene saturation in isom reduces efficiency
FCC Naphtha: Prevalent Practice

Typical Gasoline Desulfurization Process

Hydrotreating and reforming FCC naphtha destroys the valuable olefins

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## 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 vol%</th>
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</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>
</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>
</tr>
<tr>
<td><strong>subtotal</strong></td>
<td><strong>1.71</strong></td>
<td><strong>11.54</strong></td>
<td><strong>21.88</strong></td>
<td><strong>0.31</strong></td>
<td><strong>0.00</strong></td>
<td><strong>35.44</strong></td>
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<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>
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<tr>
<td>C7</td>
<td>0.68</td>
<td>1.69</td>
<td>2.46</td>
<td>1.72</td>
<td><strong>11.02</strong></td>
<td>17.57</td>
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<tr>
<td>C8</td>
<td>0.36</td>
<td>1.34</td>
<td>0.98</td>
<td>1.04</td>
<td><strong>12.30</strong></td>
<td>16.02</td>
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<tr>
<td>C9</td>
<td>0.14</td>
<td>0.67</td>
<td>0.06</td>
<td>0.29</td>
<td><strong>8.58</strong></td>
<td>9.74</td>
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<td><strong>subtotal</strong></td>
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<td><strong>8.07</strong></td>
<td><strong>9.38</strong></td>
<td><strong>4.55</strong></td>
<td><strong>36.14</strong></td>
<td><strong>60.07</strong></td>
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<td>0.11</td>
<td>0.33</td>
<td>0.01</td>
<td>0.00</td>
<td>3.35</td>
<td>3.80</td>
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<td>0.19</td>
<td>0.00</td>
<td>0.00</td>
<td>0.32</td>
<td>0.60</td>
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<td>C12</td>
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<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.15</td>
<td>0.20</td>
</tr>
<tr>
<td><strong>subtotal</strong></td>
<td><strong>0.20</strong></td>
<td><strong>0.57</strong></td>
<td><strong>0.00</strong></td>
<td><strong>0.00</strong></td>
<td><strong>3.82</strong></td>
<td><strong>4.59</strong></td>
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<tr>
<td><strong>Total</strong></td>
<td><strong>3.84</strong></td>
<td><strong>20.18</strong></td>
<td><strong>31.26</strong></td>
<td><strong>4.86</strong></td>
<td><strong>39.96</strong></td>
<td><strong>100.00</strong></td>
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</table>
FCC Naphtha: Prevalent Practice

- FCC Naphtha
- Selective Hydrogenation Unit
  - LCN
  - C5-iC6°C
  - MCN
  - 70-150°C
  - HCN
  - 150°C - EP
- GT-BTX Plus®
  - De-sulfurized Olefin-rich Raffinate
  - Various Destinations
  - Aromatics to PX Complex
- HDS
  - ULS Gasoline
- Recycle to FCC
  - ULS Gasoline

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GT-BTX PluS®: What’s in the box?

FCC Naphtha → Selective Hydrogenation Unit

- LCN
- C5-70
- MCN 70-150°C
- HCN 150°C - EP

→ Raffinate: Paraffins + Olefins*
→ Extract: Sulfur + Aromatics

H2S → H2 → Sulfur

→ Aromatics
→ ULS Gasoline
→ Recycle to FCC

GT-BTX PluS®

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GT-BTX® - General Flow Scheme

MCN Feed
Lean solvent

Extractive Distillation Column (EDC)
Aromatics-rich solvent

Olefins Rich Raffinate

Solvent Recovery Column (SRC)

Aromatics plus Sulfur to HDS

Aromatics Rich Stream

Techtiv® DS

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Petrochemical Production with GT-BTX PluS® - Aromatics

Crude Oil → Crude Distillation

- Wide Naphtha Range
- Kerosene
- Gasoil

Crude Distillation:

- Hydrotreating
- Isomerization
- Naphtha Reforming
- Desulfurization
- FCCU
- GT-BTX PluS®

_isomerization

Aromatics Plant:

- Benzene
- Toluene
- Xylenes
- Heavy Aromatics

Fuel → Gasoline

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Petrochemical Production with GT-BTX PluS® - More Aromatics

Crude Distillation

Wide Naphtha Range

Hydrotreating

Isomerization

Gasoline

Benzene

Toluene

Xylenes

Heavy Aromatics

Naphtha Reforming

Desulfurization

Kerosene

Gasoil

FCCU

FCC Naphtha

GT-Aromatization®

Fuel

ULS

Gasoline

GT-BTX PluS®

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Refinery Configuration with GT-BTX PluS® to Facilitate Increased Propylene

Crude Distillation

- Wide Naphtha Range
  - Hydrotreating
  - Naphtha Reforming
  - Desulfurization
  - FCCU
  - GT-BTX PluS®

- Kerosene
- Gasoil
- Olefinic Raffinate
- Additional Propylene
- ULS Gasoline

Extends Range of FCC Naphtha Recycle

Crude Oil

Gasoline

Fuel

Aromatics

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GT-BTX PluS®: Olefinic Raffinate to Gasoline Pool

FCC Naphtha → LCN
C5-iC6* → Raffinate: Paraffins + Olefins*
MCN 70-150°C → HCN 150°C - EP

Extract: Sulfur + Aromatics
HDS
Sulfur
H₂ H₂S

Solvent
Aromatics

Leonard's Technology

High octane low sulfur gasoline stream

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GT-BTX PluS® - Enabling Technology

Refinery  \(\xrightarrow{\text{Integration}}\)  Petrochemicals

Cat Cracking \(\xrightarrow{C4s} \) Aromatization

GT-BTX PluS  \(\xrightarrow{\text{High Octane, Low Sulfur}}\)  Gasoline

Aromatics  \(\xrightarrow{\text{Olefins}}\)  Propylene

More  Benzene  PX  More

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GT-BTX PluS® - Enabling Technology

Technically advanced extraction process enables
• FCC Gasoline Desulfurization with minimum octane loss
• Refinery Petrochemical Integration beyond Olefins
• Operational flexibility based on shifting market demands
• Maximum value upgrade to FCC naphtha
• There are over 50 references for GT-BTX family of technologies.

Patented process – available through GTC Technology

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Aromatics and Sulfur
Extraction from FCC Gasoline

Tomorrow’s Innovation Today  September 24, 2018 • Houston, Texas

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