Naphtha Valorization to its Highest Value

Presented at IOCL Petrochemical Conclave by
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Refiners have opportunity to upgrade naphtha into higher-value blendstock or petrochemicals.

By-product naphtha from cracking processes have great potential for upgradation.

Molecule management is the key to understanding the best method to process the naphtha.
Conventional Refinery Naphtha Utilization

Straight Run (Paraffins) → Typical disposition

Thermal or Catalytic Cracked (Olefins) → Fuels or Gasoline
Technology Options for Straight Run Gasoline

- **Isomalk-3**: n-C4 → i-C4
- **Isomalk-2**: Light Naphtha → C5/C6 Isomerate and Food Grade Hexane
- **Isomalk-4**: C7 Paraffins → C7 Isomerate
- **Semi-Regenerative Reforming**: Heavy Naphtha → Reformate
C5/C6 Isomerisation: Technology Choices

Three light gasoline isomerization processes

- **Zeolite catalysts**
  - High operating temperature
  - Less favorable for formation of high-branched isomers

- **Chlorinated aluminum oxide catalysts**
  - Reasonable octane increase
  - Regular organochloride additions required
  - Spent caustic disposal also required
  - Extreme measures for $\text{H}_2\text{O}$ and impurity removal

- **SI-2 Mixed metal oxide catalysts**
  - Advantages over chlorinated aluminum and zeolite, with none of the disadvantages

<table>
<thead>
<tr>
<th>Technology</th>
<th>Performance</th>
<th>Robust Operation</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite</td>
<td></td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Chlorinated Alumunim</td>
<td>✔</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isomalk-2$^{\text{SM}}$</td>
<td>✔</td>
<td></td>
<td>✔</td>
</tr>
</tbody>
</table>
Case study, World-Scale Grass-Root Isomalk-2SM Unit.

<table>
<thead>
<tr>
<th>Process scheme</th>
<th>Full Recycle Scheme (DIP, DIH, DP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity, t/y</td>
<td>1.0 MMTA</td>
</tr>
<tr>
<td>Isomerate yield, %</td>
<td>99</td>
</tr>
<tr>
<td>i-Pentane cut, RON</td>
<td>92.0-93.0</td>
</tr>
<tr>
<td>Light Isomerate, RON</td>
<td>91.5-92.5</td>
</tr>
<tr>
<td>Space velocity in the reactor block, hour(^{-1})</td>
<td>2.0 - 2.5</td>
</tr>
<tr>
<td>Start-up year</td>
<td>November, 2010</td>
</tr>
</tbody>
</table>

First World-Scale isomerization unit to use non-chlorinated catalyst and achieve 92.5 RON for final isomerate
Typical BFD for Processing Light and Heavy Naphtha

Hydrotreatment Unit

IBP - 80°C (C₇ < 2%)

Fractionation Column

IBP - 180°C

(С₆ < 0.5%)

80 - 180°C

Hydrocarbon Gas

Hydrogen Gas

Isomerization Unit

Yield: 97%

Aromatics: 0%

RON 90

24.2%

Reforming Unit

Yield: 88%

Benzene: 2%

Aromatics: 7%

RON 100

60%

Blending Section

RON 94.4

Benzene: 1.4%

Aromatics: 42.7%

Yield: 86%

Feed

100%

25%

75%
BFD for naphtha processing with C₇ isomerization technology available

Hydrotreatment Unit

Feed

Fractions:
- IBP - 70°C (C₇ < 1%)
- 70 - 105°C: 23%
- 105 - 180°C (C₆ < 0.3%): 67%

Isomerization Unit
Yield: 98%

Isomerization Unit
70-105°C Fraction
Yield: 93%

Reforming Unit
Yield: 88%

Hydrocarbon Gas

RON: 91
Aromatics: 0%
ISOMERATE 22.5%

Hydrocarbon Gas

RON: 85
Aromatics: 0%
ISOMERATE 9.3%

Benzene: 1.2%
Aromatics: 60%
REFORMATE 56.3%

Blending Section
RON 95-98
Benzene: 0.9%
Aromatics: 33.8%
Yield: 88%

Hydrotreatment Unit

Feed

Hydrogen Gas

Fractionation Column

Yield: 98%

Yield: 98%

Yield: 88%
Comparison of the 2 process configurations

From a recent case study made for a plant with light naphtha Isomerization unit (DIP, Super DIH) and CCR Reforming unit for a 2 MMTA naphtha stream.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Conventional</th>
<th>With Isomalk-4&lt;sup&gt;SM&lt;/sup&gt;</th>
<th>Benefit</th>
<th>Value to Refinery Per Annum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall gasoline yield, wt.%</td>
<td>88.7%</td>
<td>90.8%</td>
<td>2.1%</td>
<td>16.8 MM USD *</td>
</tr>
<tr>
<td>Octane Number, RON</td>
<td>94.0</td>
<td>95.5</td>
<td>1.5</td>
<td>15.0 MM USD *</td>
</tr>
<tr>
<td>Benzene in the gasoline pool, vol.%</td>
<td>1.5%</td>
<td>0.6%</td>
<td>0.9% less</td>
<td>Varies</td>
</tr>
<tr>
<td>Aromatics in the gasoline pool, vol.%</td>
<td>37.0%</td>
<td>33.5%</td>
<td>3.5% less</td>
<td>Varies</td>
</tr>
</tbody>
</table>

Total benefit is over 30 MM USD/yr with the C<sub>7</sub> paraffins routed to Isomalk-4<sup>SM</sup>.

* - based on $400/ton differential for liquid yield over gas; and $5/ton-octane number
Tailoring the feed may be useful

Steam Cracker

Dearomatization (GT-DeArom\textsuperscript{sm})

BTX+

\text{C2=, C3=, BD, Bz, H}_2
Cracked Gasoline Management – FCC Desulfurization

Conventional Three-Stage Process

FCC Naphtha → LCN C5-iC6⁻ (optional) → Caustic Extraction

MCN 70-150°C → Medium HDS

HCN 150°C-EP → Severe HDS

C₆-C₉ Olefins (Saturation (unavoidable)) → medium HDS

Sulfur (Desulfurization (needed)) → Severe HDS

ULS Gasoline

ULS Gasoline

ULS Gasoline

ULS Gasoline

MCN 70-150°C

LCN C5-iC6⁻
Alternate Option to Extract Sulfur from the Olefins

FCC Gasoline Desulfurization

- FCC Naphtha
- LCN C5-iC6-
  (optional)
- MCN 70-150°C
- HCN 150°C-EP
- Caustic Extraction
  Medium HDS
  Solvent
  Raffinate: Paraffins + Olefins
- Mild HDS
  Extract: Sulfur + Aromatics
  Aromatics
- HDS
  \( \text{H}_2 \) \( \text{H}_2 \text{S} \)
- Severe HDS
  ULS Gasoline

GT-BTX PluS®
GT-BTX PluS® - Enabling Technology

- 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
Typical Refinery Configuration with GT-BTX PluS® - Products to Gasoline

- Zero Δ in octane value
- Low benzene
- Low sulfur
Refinery Configuration with GT-BTX PluS® to facilitate increased Propylene

Extends Range of FCC Naphtha Recycle
Economical Ethylene Capacity for Recovering By-products

Ethylene rate, KTA
(Liquids feed)

- Ethylene, Propylene, Primary Derivations
- Butadiene, Benzene, Toluene, Xylenes
- Styrene Extraction, C9 Resins
- Isoprene, DCPD, Pips
- Naphthalene, Secondary Deriv.

Economical to Produce

200 400 600 800 1000 1200 1400
Pygas C5 Utilization – GTC GT-C5/Isoprene

Raw C5

Lights Removal Section

Dimerization Section

C5 Splitter Section

Extraction Section

PIPS and DCPD Finishing Section

Finishing Section

Lights

Mono Olefins/ Paraffins

High Purity Isoprene

C6 Stream

PIPS

60 – 75 %DCPD

85 %DCPD

Raw C5
Extractive Distillation depends on a selective solvent to alter the boiling points of aromatics & non-aromatics to facilitate their separation by distillation.

Solvent selectivity is critical

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\alpha$ n-C7/Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Techiv-100\textsuperscript{im}</td>
<td>2.44</td>
</tr>
<tr>
<td>Sulfolane</td>
<td>2.00</td>
</tr>
<tr>
<td>N-methyl Pyrolidone</td>
<td>1.95</td>
</tr>
<tr>
<td>N-formyl Morpholine</td>
<td>1.89</td>
</tr>
<tr>
<td>Glycol blends</td>
<td>1.35</td>
</tr>
<tr>
<td>None</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Proprietary solvent of GT-BTX\textsuperscript{®} Technology
Benzene, Toluene, Xylene need to be extracted from C6 – C8 cut of pygas in order to meet petrochemical quality.

Clariant catalysts available for both stages of Pygas HDT.
World-Class Extraction Technology
for BTX Purification

Hydrocarbon Feed

Lean solvent

Extractive Distillation Column (EDC)

Aromatics rich solvent

Raffinate

Solvent Recovery Column (SRC)

Aromatics to downstream fractionation
Pygas C8 Utilization – GT-Styrene

Heart cut distillation followed by ED

Pygas → C8 → Light Cut → GT-Styrene® → 99.8+ wt.% Styrene

C5, C6, C7 → C8 Cut → Heavy Cut

C9, C10
Pygas C8 Utilization – GT-Styrene

Recovery of styrene from the raw pyrolysis gasoline derived from the steam cracking of naphtha, gas oils, and natural gas liquids (NGL)
## Economics of Styrene Recovery
**Basis - 25,000 mt/yr Styrene (2014 pricing)**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>GT-Styrene®</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital cost</td>
<td>$28 MM</td>
</tr>
<tr>
<td>Feedstock cost, $/ton</td>
<td>$600</td>
</tr>
<tr>
<td>Processing cost, $/ton</td>
<td>$200</td>
</tr>
<tr>
<td>Total production cost, $/ton</td>
<td>$800</td>
</tr>
<tr>
<td>Sales price, $/ton</td>
<td>$1250</td>
</tr>
<tr>
<td>Net margin</td>
<td>$11.25 MM</td>
</tr>
<tr>
<td>Pre-tax ROI</td>
<td>40%</td>
</tr>
</tbody>
</table>
Pygas C9+ Utilization – Naphthalene, Solvent, & Resin

PGO Feed → Lights Removal Column → Water, C9 to HCR Feed → Naphthalene Fractionator

Naphthalene Fractionator → Purification System → Finishing Section → Solvent Flasher

Purification System → Naphthalene

Finishing Section → Solvent, PFO or Fuel

Solvent Flasher → Naphthalene, Solvent, & Resin
The nature of raw materials leads to proper processing scheme

Non-chlorinated isomerization catalysts are the optimum to boost gasoline octane for C4 – C7 fractions of straight run gasoline

Refinery/petrochemical integration, in addition to propylene recovery, captures aromatics and preserves olefins from FCC gasoline

Steam cracker by-products are important to recover from large plants using naphtha feedstock

Technology is available to upgrade products from C4 – C12 boiling range