Mr. Joseph C. Gentry

Director, Global Licensing
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- Mr. Joseph earned a BS degree in chemical engineering from Auburn University and an MBA from the University of Houston. He is the inventor of several patented separations technologies and has specialized in the application of these for the petrochemical industry.

- He has previously worked for ARCO Chemical Company, and Lyondell Petrochemical Company as a process engineer in the olefins and aromatics areas and has authored several papers on licensing process technologies in refining and petrochemical applications.

- He is a specialist in GT-BTX and GT-Styrene, working in all areas of Technology, Licensing and Business Development.
Unlocking Value Potential from Naphtha Cracker By-Product Streams

Joseph C. Gentry • Director, Global Licensing

IOCL 2013 Petrochemical Conclave
March 18, 2013
Introduction to GTC Technology

- Technology and global licensor for innovative solutions in:
  - Petrochemicals
  - Chemicals
  - Refining
  - Gas processing/Sulfur

- Global headquarters - Houston, Texas

- Regional subsidiaries in China, Korea, India, Singapore, the Czech Republic and Mexico

- Separations and Mass Transfer Solutions

- Process know-how, engineering, equipment, critical chemicals/catalysts and services
“I used to do pretty well just focusing on ethylene and propylene.

“Now I have to recover as many of the heavier co-products as I can to stay competitive globally.

“Increased competition from producers with cost advantaged feedstock and shale gas ethane in North America has not helped.

Fortunately my naphtha cracker makes some higher value products in the Py-gas stream.

I wonder if I can separate and market them?”

Searching for added value in C5 – C12 Py-gas from the cracker
## Typical Product Slate from Naphtha Cracker

<table>
<thead>
<tr>
<th>Product</th>
<th>Ethane</th>
<th>Propane</th>
<th>Butane</th>
<th>Naphtha</th>
<th>Atmospheric Gas Oil</th>
<th>Vacuum Gas Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen - 95%</td>
<td>9</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Methane</td>
<td>7</td>
<td>28</td>
<td>22</td>
<td>17</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>Ethylene</td>
<td>78</td>
<td>42</td>
<td>40</td>
<td>34</td>
<td>26</td>
<td>21</td>
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<tr>
<td>Propylene</td>
<td>2</td>
<td>17</td>
<td>17</td>
<td>16</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>Butadiene</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Pyrolysis Gasoline, including:</td>
<td>1</td>
<td>7</td>
<td>7</td>
<td>19</td>
<td>18</td>
<td>19</td>
</tr>
<tr>
<td>Piperylene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.4</td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td>Isoprene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.9</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Benzene</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>7</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Toluene</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Xylene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td>Styrene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td>Other, C9+</td>
<td>0</td>
<td>3</td>
<td>1</td>
<td>6</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>18</td>
<td>25</td>
</tr>
<tr>
<td>Balance</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>11</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

*Values obtained at high severity and with recycling unconverted E/P Stream, Chauvel & Lefebvre 1989*
GTC Portfolio in Refining, Petrochemical, Gas Processing/Sulfur & Polyester Industries

**Crude Distillation**
- Crude Oil
  - Heavy Naphtha
  - Light Naphtha
  - Kerosene
  - Gasoil

**Steam Cracker Petrochemical Complex**
- Natural Gas
  - NGL
- Sulfur

**C4 Processing**
- Isoprene
- Piperylene
- DCPD, HCR

**Aromatization**
- Benzene, Toluene
- Xylene (BTX)

**Styrene Recovery**
- Styrene

**PGO Processing**
- Naphthalene
- Resin Oil

**Hydrotreating**
- Heavy Aromatics

**BTX Recovery**
- Benzene
- Toluene
- Xylenes

**Disproportionation**
- MeOH
- Alkylation

**Paraxylene Recovery**
- Crystallization/Hybrid

**Isomerization**

**DX Process**
- Fuel

**Paraxylene**
- PTA (IPA)
- DMT (DMI)

**Polyester Chip**

**Sulfur Recovery Unit**
- Sulfur
Unlocking Value in the Py-gas Stream from every carbon molecule, C5-C12

C5 – Diolefins
- Piperylene (1,3 pentadiene) “Pip’s” → Hydrocarbon Resin “HCR”
- DCPD → HCR, Unsaturated Polyester Resin
- Isoprene → Rubber

C6 - Benzene → EB → Styrene

C7 – Toluene
- Xylenes
- Toluene (Methylation with MeOH) → Paraxylene

C8 – Xylenes → Paraxylene → PTA → Polyester
- Styrene (Extraction) → SBR, PS, Rubber

C9 – Resin Oil → HCR → Inks, Adhesives

C10 – Naphthalene → Naphthenic Derivatives

C11–C12 – Aromatic Solvents
Economical Ethylene Capacity for Recovering By-products

- Ethylene, Propylene, Primary Derivations
- Butadiene, Benzene, Toluene, Xylenes
- Styrene Extraction, C_9 Resins
- Isoprene, DCPD, Pips
- Naphthalene, Secondary Deriv.

Ethylene rate, KTA (Liquids feed)
Primary By-products from Pygas

- **Isopentane**
  - C₅ to recycle cracking

- **High-purity Isoprene**
  - 99 wt. %

- **Piperylenes**
  - High-purity DCPD 70 to 85 wt. %

- **Benzene**
  - Toluene
  - Xylenes

- **High-purity Styrene**
  - 99.9 wt. %

- **Resin Oil**
  - Naphthalene
  - Aromatic Solvents

**Raw Pyrolysis Gasoline**

- **C₅ Fraction**
  - Pygas Hydrotreating
    - GT-BTX Select ®
      - Benzene
      - Toluene
      - Xylenes
    - GT-Styrene®
      - High-purity Styrene 99.9 wt. %

- **C₆⁺ fraction**
  - Resin Oil
    - Naphthalene
    - Aromatic Solvents

- **PGO/PFO (Fuel Stream)**

Naphtha Cracker By-products – C5s

- For naphtha cracking, by-product C5s are of 0.13-0.18 /ton of ethylene
- Diolefin C5 petrochemicals have much higher value than hydrotreating and recycle cracking
- Composition of C5s from a high severity naphtha cracker:
  - 15% isoprene
  - 16% CPD, DCPD
  - 11% pips
  - 8% n-pentene
  - 11% isopentene
  - 4% cyclopentane, cyclopentene
  - 33% pentanes
  - 2% acetylenes, others
Naphtha Cracker By-products – C5s Molecules and Applications

**Primary Components of Interest**

- Isoprene - 2 methyl-1,3 butadiene
- Piperylenes - cis, trans/1,3 pentadiene
- CPD - cyclopentadiene
- DCPD - dicyclopentadiene

**Other Components**

- Isopentane- Gasoline blend-stock
- C5 Mono-olefins - TAME, catalytic cracking, aromatization, resin feedstock
- Paraffins - Solvents, refrigeration, cracker feed
C5 Separation

C5 Feed → C5 splitting / Dimerization

→ DCPD and PIPS

→ Isoprene Extraction

→ Isopentane

→ IPR - polymer Grade

→ C5 Paraffins & Mono Olefins

→ PIPS

→ DCPD (70 - 99%)

→ Heavies (Oligomers & Polymers)
C5s to HCR
Benefits of GTC’s Advanced C5 Process

• Lower energy and capital cost for C5 separation
  • Improved CPD/DCPD dimerization
  • State-of-the-art separation
  • High value intermediates created for HCR

• Integrated C5 recovery/HCR product synergies
  • Improved feedstocks enhance performance of the HCRs
  • Improved system economics via pipeline return of non-reactives
  • Option for product off take of PIP’s and DCPD, with optional production of isoprene if desired
  • Reduced energy and capital by matching PIP/DCPD spec to HCR plant needs
Naphtha Cracker By-products – BTX

Liquid-Liquid Extraction

Extractive Distillation

- Feed
- Solvent
- H₂O
- Raffinate
- Aromatics Extract
- EDC
- SRC
- Raffinate
- Aromatics Extract

Heartcut distillation followed by ED

Pygas → C5 → C6 → C7 → C8 → Light Cut → C8 Cut → GT-Styrene® → 99.9 wt.% Styrene

C8 → C9 → C10 → Heavy Cut
<table>
<thead>
<tr>
<th>Parameters</th>
<th>GT-Styrene®</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital Cost</td>
<td>$30 MM</td>
</tr>
<tr>
<td>Net Feedstock Cost, $/ton</td>
<td>$800</td>
</tr>
<tr>
<td>Processing Cost, $/ton</td>
<td>$250</td>
</tr>
<tr>
<td>Total Production Cost, $/ton</td>
<td>$1050</td>
</tr>
<tr>
<td>Sales Price, $/ton</td>
<td>$1550</td>
</tr>
<tr>
<td>Net Margin</td>
<td>$12.50 MM</td>
</tr>
<tr>
<td>Pre-tax Contribution Margin</td>
<td>42%</td>
</tr>
</tbody>
</table>

- Basis: 25,000 MT/yr Styrene
Pygas Byproducts – C9 – C12
Naphthalene & Aromatic Solvents

- C9s - Hydrocarbon resin feedstock
- C10 – Naphthalene and derivatives (additive for concrete modifiers)
- C11 & C12 - Heavy aromatic solvents
## Summary of Upgrade Options

<table>
<thead>
<tr>
<th>C5 - C12</th>
<th>Product Area</th>
<th>Capital MM$</th>
<th>~ Payback (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
<td>Piperylene/DCPD - GT-C5 for HCR GT-Isoprene™</td>
<td>25</td>
<td>3</td>
</tr>
<tr>
<td>C6</td>
<td>Benzene (GT-BTX®)</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>C7</td>
<td>Toluene (GT-BTX®) GT-TolAlk™</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>C8</td>
<td>Styrene (GT-Styrene®)</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>C9</td>
<td>Resin Oil, Solvents</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>C10</td>
<td>Naphthalene, Solvents</td>
<td>15</td>
<td>2</td>
</tr>
<tr>
<td>C11 - C12</td>
<td>Aromatic Solvents</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

GTC Technology is the only global licensor which offers all required technologies, and can assist in product placement.