Valuable Chemicals From Cracker Pygas
Maintain Competitiveness for Naphtha Crackers

SULZER GTC Technology US, INC
Economical Ethylene Capacity for Recovering By-products

- Ethylene, Propylene, Primary Derivations
- Butadiene, Benzene, Toluene, Xylenes
- Styrene Extraction, C3 Resins
- Isoprene, DCPD, Pips
- Naphthalene, Secondary Deriv.

Ethylene rate, KTA (Liquids feed)

Economical to Produce
Naphtha Cracker Byproducts – Pygas
GTC- Offered Overall Processing Scheme

- Crude Isoprene Extraction
  - High-Purity Isoprene
  - High-Purity DCPD/PIPs

- GT-BTX®
  - Benzene
  - Toluene
  - Xylenes

- GT-Styrene®
  - High-purity Styrene 99.9 wt. %

- Aromatic Resins

- High-Purity Naphthalene
  - High-purity Naphthalene 99.0 wt. %

- Pygas HDT
  - Isopentane
  - C₅ to recycle cracking
  - High-purity Isoprene 99 wt. %

- Piperylenes
  - High-purity DCPD 95 wt. %

- C₅ Fraction

- C₆₊ Fraction

- Raw Pyrolysis Gasoline
Pygas C5 Utilization

Primary Components of Interest

- Isoprene  
  (2 methyl 1, 3 butadiene)

- Piperylenes  
  (cis & trans 1, 3 pentadiene)

- CPD  
  (cyclopentadiene)

- DCPD  
  (dicyclopentadiene)

Other Components

- Isopentane  
  Gasoline blendstock

- C5 Mono-olefins  
  TAME, cracking, aromatization, resins

- Paraffins  
  Cracker feed
Pygas C5 Utilization – GTC GT-C5/Isoprene

- **Lights Removal Section**
- **Dimerization Section**
- **C5 Splitter Section**
- **Extraction Section**
- **Finishing Section**

**Flow Diagram**:
- **Raw C5** → **Lights Removal Section** → **Dimerization Section** → **C5 Splitter Section** → **Extraction Section** → **Finishing Section** → **Lights**
- **High Purity Isoprene**
- **Mono Olefins/ Paraffins**
- **C6 Stream**
- **PIPS**
- **60 – 75 %DCPD**
- **85 %DCPD**

**Notes**:
- PIPS and DCPD Finishing Section
Pygas C5 Utilization – GTC GT-C5

C5s → Lights Removal → C5 Splitter → Dimer → Crude Isoprene Product 32% → PIPS → Heavies

Sulfur Removed → PIPS → Dimer → C6 Purge

Crude Isoprene Product 32%

Lights Removal

C5 Splitter

Dimer

Heavies

DCPD 70%

DCPD 85%

C6 Purge
• Use of Techiv® 600 avoids toxicity and corrosive issues of traditional ACN, NMP, and DMF
• Acetylene hydrogenation simplifies process to one-stage ED/SRC
• Process can produce isoprene at 80% or 99.5+% purity
Pygas C5 Utilization – GTC GT-C5

- Lower energy and capital cost for C\textsubscript{5} separation
  - Improved CPD/DCPD dimerization
  - State of the art separation
  - High value intermediates created for HCR

- High Selectivity catalyst used for selective acetylene hydrogenation

- Integrated C\textsubscript{5} recovery/HCR Product synergies
  - Improved feedstocks enhance performance of the HCRs
  - Improved system economics return of non-reactives
  - Guaranteed product off take for Pips and DCPD, with optional production of isoprene if desired
  - Reduced energy and capital by matching Pips & DCPD specs to HCR plant needs
Pygas Upgrade

C6-C8 UTILIZATION
Pygas C6-C8 Utilization

Benzene, Toluene, Xylene need to be extracted from C6 – C8 cut of pygas in order to meet petrochemical quality.
# Pygas C6-C8 Utilization

## Technologies for BTX Extraction

<table>
<thead>
<tr>
<th>Liquid-Liquid Extraction (LLE)</th>
<th>Extractive Distillation (ED)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional and out-dated</td>
<td>Most recent technology</td>
</tr>
<tr>
<td>More &amp; larger equipment</td>
<td>Less &amp; smaller equipment</td>
</tr>
<tr>
<td>Higher capital and larger plot size</td>
<td>Lower capital and smaller plot size</td>
</tr>
<tr>
<td>Higher utility consumption</td>
<td>Lower utility consumption</td>
</tr>
<tr>
<td>Complicated control</td>
<td>Simple control, easier to operate</td>
</tr>
<tr>
<td>Corrosion</td>
<td>None</td>
</tr>
</tbody>
</table>
Pygas C6-C8 Utilization

LLE vs ED

Liquid-Liquid Extraction

Extractive Distillation

H₂O

Raffinate

Aromatics Extract

Solvent

Feed

EDC

SRC

Raffinate

Aromatics Extract

Solvent

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

Proprietary solvent of GT-BTX® Technology

Solvent selectivity is critical

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\alpha$ $n$-$C_7$/Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Techti®-500</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>
Pygas Upgrade

C8 UTILIZATION
Styrene And Close-boiling Pygas Components

- **Styrene**
  - NBP 145°C

- **Ethylbenzene**
  - NBP 136°C

- **Orthoxylene**
  - NBP 144°C

- **Phenyl Acetylene**
  - NBP 142°C

- **Dicyclopentadiene**
  - NBP 152°C

- **Cumene**
  - NBP 152°C
Separation Between Styrene and Close-boiling Components

- Solvent-based system to extract and purify styrene
- Extractive distillation alters boiling points of components

<table>
<thead>
<tr>
<th>Component</th>
<th>NBP (°C)</th>
<th>Relative volatility to Styrene</th>
<th>Relative volatility to Styrene (Enhanced)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>145</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>136</td>
<td>1.3</td>
<td>2.6</td>
</tr>
<tr>
<td>Ortho-xylene</td>
<td>144</td>
<td>1.0</td>
<td>1.8</td>
</tr>
<tr>
<td>DCPD</td>
<td>152</td>
<td>0.6</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Heart cut distillation followed by ED

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

- C₅
- C₆
- C₇
- C₈ Cut
- C₉
- C₁₀

Light Cut

Heavy Cut
Pygas C8 Utilization – GT-Styrene®

- Pyrolysis Condensates
- DeC₄
- DeC₅
- Crude C₄S
- Raw C₅S
- 1st Stage
  - H₂
  - GT-Styrene®
  - DeC₇
- 2nd Stage
  - H₂
  - H₂S
  - GT-BTX®
  - DeC₈
  - C₉+
- Raffinate C₆ – C₈
- Benzene
- Toluene
- Xylenes
- Styrene

- ☀ Catalyst life extended
- ☀ H₂ consumption reduced to ~half
- ☀ High value SM product
- ☀ Upgrade from solvent-grade to PX production feed
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)
Styrene Monomer product shall meet the general standard specification for Styrene ASTM D2827-13 as follows:

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Specification</th>
<th>ASTM Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Pt/Co scale</td>
<td>15 max</td>
<td>D5386</td>
</tr>
<tr>
<td>Styrene purity</td>
<td>wt%</td>
<td>99.8 min</td>
<td>D5135 or D7504</td>
</tr>
<tr>
<td>Aldehydes (as benzaldehyde)</td>
<td>wt%</td>
<td>0.01 max</td>
<td>D2119 or D7704</td>
</tr>
<tr>
<td>Peroxides (as H₂O₂)</td>
<td>mg/kg</td>
<td>50 max</td>
<td>D2340</td>
</tr>
<tr>
<td>Polymer</td>
<td>mg/kg</td>
<td>10 max</td>
<td>D2121, Test Method A</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>mg/kg</td>
<td>10-15</td>
<td>D4590</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>mg/kg</td>
<td>500 max</td>
<td>D5135 or D7504</td>
</tr>
<tr>
<td>Benzene</td>
<td>mg/kg</td>
<td>1 max</td>
<td>D6229</td>
</tr>
<tr>
<td>Appearance</td>
<td></td>
<td>Clear liquid free of sediment and haze at 65 (18 °C) to 78°F (25 °C)</td>
<td></td>
</tr>
</tbody>
</table>
- Produces polymer-grade styrene at 99.8+% purity
- Allows the recovery of low EB-content mixed xylenes for paraxylene production
- Debottlenecks pygas hydrotreater and extends cycle length
- Reduces hydrogen consumed in hydrotreating
- Optimized solvent system and design provide economical operating costs
Basis: 30,000 tpa styrene

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical USGC grassroots capital cost (ISBL)</td>
<td>$40 million</td>
</tr>
<tr>
<td>Styrene value in pygas</td>
<td>$600/ton</td>
</tr>
<tr>
<td>Styrene product sales value</td>
<td>$1300/ton</td>
</tr>
<tr>
<td>Net processing cost</td>
<td>$200/ton</td>
</tr>
<tr>
<td>Net profit</td>
<td>$14 million/yr</td>
</tr>
<tr>
<td>Simple annual ROI</td>
<td>35%</td>
</tr>
</tbody>
</table>

- Existing HDT greatly debottlenecked for lower H2 consumption and longer catalyst life
- Additional value for xylenes upgrade
• GT-Styrene® technology - effective complement to world-scale naphtha crackers
• GT-Styrene® provides excellent value for steam crackers which produce more than 600,000 tpa ethylene, based on liquid feedstock or 1,200,000 tpa ethylene from a typical mixed feedstock
• Reduced-EB xylenes available as co-product of GT-Styrene®
• H₂ consumption is reduced using GT-Styrene®
• 6 licensed units, 3 in operation for more than 5 years
Pygas Upgrade

C9+ UTILIZATION
Pygas C9+ Utilization – Naphthalene, Solvent, & Resin

Lights Removal Column
PGO Feed

Naphthalene Fractionator
C9 to HCR Feed
Water

Purification System

Finishing Section
Naphthalene

Solvent Flasher
Solvent
PFO or Fuel
# Pygas Upgrade Summary

## Summary of Upgrade Options

<table>
<thead>
<tr>
<th>C5 - C12</th>
<th>GT-Product Area</th>
<th>Capital MM$</th>
<th>~ Payback (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
<td>Piperylenes/DCPD : GT-C5 for HCR GT-Isoprene™</td>
<td>25, 35</td>
<td>3</td>
</tr>
<tr>
<td>C6-C8</td>
<td>Benzene, Toluene, Xylenes (GT-BTX®)</td>
<td>25, 25</td>
<td>2</td>
</tr>
<tr>
<td>C8</td>
<td>Styrene (GT-Styrene®)</td>
<td>40</td>
<td>2.5</td>
</tr>
<tr>
<td>C9</td>
<td>Resin Oil, HCRs</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>C10</td>
<td>Naphthalene</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’s cutting-edge technologies and innovative process design help the liquid crackers greatly improve the economics and competitiveness.