Dominant Technology for the Propylene Production (DTP®) Process

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2: Mitsubishi Chemical Corporation
Contents

- Why propylene?
- DTP® Process Features
- DTP® Demonstration Plant Running
- Development Schedule
Propylene is an important intermediate product.
World Demand for Propylene

Unit: $\times 10^6$ ton

‘08-’14 Increase 4.2%/year

## Conventional Propylene Production Process

<table>
<thead>
<tr>
<th>Process</th>
<th>Cracking (Fluid Catalytic Cracking)</th>
<th>FCC</th>
<th>DCC [S&amp;W]</th>
<th>OLEFLEX [UOP]</th>
<th>OCT [ABB Lummus]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock</td>
<td>Light Naphtha</td>
<td>VGO</td>
<td>85%VGO+ 15%VR</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;= &amp; 2-C&lt;sub&gt;4&lt;/sub&gt;=</td>
</tr>
<tr>
<td><strong>Yield [wt%]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;=</td>
<td>29.0</td>
<td>1.0</td>
<td>3.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;=</td>
<td>18.0</td>
<td>4.7</td>
<td>22.9</td>
<td>85.0</td>
<td>&gt;90.0</td>
</tr>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;/C&lt;sub&gt;2&lt;/sub&gt;= ratio</td>
<td>0.6</td>
<td>4.7</td>
<td>6.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Production Ratio [%]</strong></td>
<td>66</td>
<td>32</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


- Almost all propylene is produced from cracking and FCC.
- Propylene is by-product of cracking and FCC.
# Ethane Crackers in the Middle East

<table>
<thead>
<tr>
<th>Country</th>
<th>Owner</th>
<th>Capacity [10^4 ton/year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iran</td>
<td>Kharg Petrochemical</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Amir Kabir Petrochemical</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>Maroon Petrochemical</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>Arvand Petrochemical</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Arya Sasol Polymer</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Jam Petrochemical</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>NPC/VPC(No.11)</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>NPC/VPC(No.12)</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Ilam Petrochemical</td>
<td>32</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>Rabigh Refining Petrochemical</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>Tasnee Petrochemical</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Eastern Petrochemical</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>Yansab</td>
<td>130</td>
</tr>
<tr>
<td>Qatar</td>
<td>Ras Laffan Ethylene</td>
<td>130</td>
</tr>
<tr>
<td>UAE</td>
<td>BOUROUGE-II</td>
<td>140</td>
</tr>
<tr>
<td>Kuwait</td>
<td>Equate-II</td>
<td>85</td>
</tr>
</tbody>
</table>

- **Total capacity for ethylene production:** 16 million ton/year

Reference: ENN (2005)
# Product Yield for Feedstock of Cracker

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Ethane</th>
<th>Propane</th>
<th>Butane</th>
<th>Naphtha</th>
<th>VGO</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂ Yield</td>
<td>53</td>
<td>40</td>
<td>33</td>
<td>32</td>
<td>22</td>
</tr>
<tr>
<td>C₃ Yield</td>
<td>1</td>
<td>14</td>
<td>18</td>
<td>16</td>
<td>12</td>
</tr>
</tbody>
</table>

![Graph showing product yield data for different feedstocks.](image)

Propylene Situation

- By-product from naphtha cracking and FCC
- Increasing demand (300 million ton/year)
- Boom in the construction of ethane crackers
- Wild fluctuations in oil prices

- Expanding of propylene demand-and-supply gap
- Diversification of raw materials

**Dominant Technology for Propylene production(DTP®)**
Lower Olefins Production from Natural Gas

Natural Gas
\[ \text{CH}_4 \]

\[ \text{C}_2\text{H}_6 \]
\[ \text{C}_3\text{H}_8 \]

\[ + \text{H}_2\text{O} \]
\[ + \text{O}_2 \]

Synthesis Gas

DME

\[ \text{DME to \ Propylene} \]

\[ - \text{H}_2\text{O} \]

Methanol

\[ \text{Methanol to \ Olefins} \]

\[ \text{Cracking} \]

\[ - \text{H}_2 \]

\[ \text{Dehydrogenation} \]

\[ - \text{H}_2 \]

Olefins

\[ \text{C}_2\text{H}_4 \]
\[ \text{C}_3\text{H}_6 \]
DTP Reaction

- **Main product**: Propylene
- **By-products**: Water, Ethylene, C\textsubscript{4}-C\textsubscript{6} Olefins, C\textsubscript{1}-C\textsubscript{4} Paraffins, C\textsubscript{7}+ Hydrocarbons etc.
Advantages of DTP® Catalyst

- Proprietary MFI type Zeolite (ZSM-5) Catalyst
- High Propylene Selectivity
- Stable Performance at High Temperature

Feed: DME

Graph showing DME conversion over time on stream for DTP® Catalyst and typical MFI catalyst.
DTP® Process Flow

**Feed:**
Methanol

2,500 t/d

- DME + Steam
- Hydrocarbon Recycle
- Dehydration Reactor
- DTP Reactor
- Water Separator
- Compressor
- Separation Unit
- C_{1-2}
- Light gas
- Propylene
  760 t/d
  (254,000 t/y)
- LPG
- C_{4-6}
- Gasoline

**Produced:**
- Gasoline
- LPG
- Propylene
- Light gas

**Other:**
- DME + Steam
- Water
DTP® Process Features

- Joint Development of JGC Corporation and Mitsubishi Chemical Corporation
- Simple Fixed-bed Adiabatic Reactor
- Catalyst Regeneration by Combustion of Coke
- High Propylene Yield (70%) by Recycling By-Products
- Optional Co-Feed of C₄ Olefins from Naphtha Cracker / FCC
DTP® Demonstration Plant

- Constructed in Mitsubishi Chemical’s Mizushima Plant
- Operation Started in August 2010

This demonstration is subsidized by NEDO.
DTP® Demonstration Plant Features

- Identical Reaction Conditions to Those of Commercial Scale Design
- Actual C₄-C₆ By-Products Recycling to DTP® Reactor
- Reactor Switching for Regeneration
- Optional Co-Feed of C₄ Olefins from Naphtha Cracker
- Confirmation of State of Products
Example of Running Data of the Demonstration Plant

Feed: Methanol

Feed: C4 Olefin

DME + Steam

Hydrocarbon Recycle

Light gas 3 %
Propylene 70 %
LPG 3 %
Purge 8 %
Gasoline 16 %

C₄-C₆

Water

High Selectivity for Propylene

Selectivity = Total Carbons of each effluent / Total carbons of methanol and C4 olefins as feed
Example of Running Data of the Demonstration Plant

Propylene Yield = Total Carbons of propylene product / Total carbons of methanol and C4 olefin as feed

Propylene Yield: approximately 70%

Propylene Yield = Total Carbons of propylene product / Total carbons of methanol and C4 olefin as feed
Example of Running Data of the Demonstration Plant

- Repeat of Reaction and Regeneration Successfully

Propylene Yield [%] vs. Days

Propylene Yield: Calculated according to products from reactor A
Confirmation of State of Products

Products from Demonstration Plant

- Propylene mixture
- Water
- Gasoline

➢ Analyzed and evaluated each product
Confirmation of State of Catalyst

Catalysts from DTP Reactor of Demonstration Plant

- Fresh Catalyst
- Degraded Catalyst
- Regenerated Catalyst

- Coke on Degraded Catalyst Eliminated Sufficiently
Propylene Production via Methanol Derived from Natural Gas in Gas-Producing Countries

Propylene Production with the Use of Both Methanol and Ineffectively Utilized C₄ Olefins from Naphtha Cracker
## Comparison with Competitive Processes

<table>
<thead>
<tr>
<th>Process</th>
<th>MTO</th>
<th>MTP</th>
<th>DTP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Company</td>
<td>UOP / Hydro</td>
<td>Lurgi</td>
<td>JGC / Mitsubishi Chemical</td>
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<tr>
<td>Catalyst</td>
<td>modified SAPO-34</td>
<td>modified ZSM-5</td>
<td>modified ZSM-5</td>
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<tr>
<td>Process description</td>
<td>Fluidized bed</td>
<td>Fixed bed</td>
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<tr>
<td>Regeneration</td>
<td>Continuous</td>
<td>Batch mode</td>
<td>Batch mode</td>
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<tr>
<td>Recycle</td>
<td>no</td>
<td>Olefin and Water</td>
<td>Olefin and Paraffin</td>
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<tr>
<td>Conversion [%]</td>
<td>99.6</td>
<td>&gt;99</td>
<td>&gt;99.9</td>
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<tr>
<td></td>
<td>Pressure[bar-G]</td>
<td>1-3</td>
<td>1.5</td>
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<tr>
<td>Olefin Yields[wt%]</td>
<td>Ethylene</td>
<td>48-31</td>
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<td>Propylene</td>
<td>34-45</td>
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# DTP® Process Development Schedule

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<td>Equipment Scale</td>
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<td>Labo. Reactor (2 g/d)</td>
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<td>Bench Plant (5 kg/d)</td>
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<td>License Promotion</td>
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</table>
Thank You for Your Attention!

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