Alternative On-purpose Production Methods for Propylene

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Lower cost ethane feed is replacing naphtha as source of feed to steam crackers

Worldwide shale gas reserves will increase this shift

This shift will reduce the supply of $C_3$ and heavier products opening up the need for greater by-product flexibility in both new and existing plants
World Cracker Feedstock Trends

World cracker feedstock is getting lighter

Source: IHS
U.S. cracker feedstock is becoming very light

Source: CMAI
Olefins Regional Average Prices

- High price for C₄
- Propylene price above ethylene price

Source: GlobalData
Summary of Supply Market Trends

- **C₄ feedstock availability**
  - Global trends indicate tightening availability of mixed C₄ from steam crackers (IHS)
  - Many new crackers on light feedstocks – ethane or LPG
  - Mixed C₄s to new butadiene extraction (BDE) units
  - Butadiene diverted from propylene production via metathesis technology

- **Declining gasoline market**
  - Efficient vehicles; expensive fuel
  - Results in less propylene produced in refinery FCCs
  - Potentially less refinery C₄s available for OCT feed
Demand Market Trends

World PG/CG* Propylene Supply and Demand

Propylene demand increase 5 – 6% per year

* Polymer Grade/Chemical Grade Propylene
World PG/CG* Propylene Production By Technology

* Polymer Grade/Chemical Grade Propylene
Propylene yield from ethane is very low

Impact on Propylene Production - Cracker Yields

- MT of Product Per MT of Ethylene
- Propylene yield from ethane is very low
The 10% shift from naphtha to ethane feed reduces available propylene production by 7.5 million MTA.

Propylene demand is expected to increase by 25 million MTA by 2019.

On-purpose propylene production will be needed to make up this shortfall.

Metathesis chemistry has and will continue to play a key role in on-purpose propylene production.
Routes to Propylene – Traditional & On-purpose

- Steam Cracker
- FCC
- Dimerization
- MTO
- Propane Dehydrogenation (PDH, on-purpose)
- Olefins Conversion Technology (OCT, on-purpose)

Propylene
Ext. of Conventional Metathesis - C<sub>5</sub>s as OCT Feedstock

Crude Fractions

Methanol-to-Olefins By-product

FCC Recovery

Steam Cracker Pyrolysis Gasoline
Why Metathesis?
Highest Propylene Yield

C₄ Metathesis Reaction

0.7 ton Butene-2 + 0.3 ton Ethylene = 1.0 ton Propylene
Highest Propylene Yield

C₅ Metathesis Reaction

Pentene-2
0.55 MT

Ethylene
0.45 MT

Propylene
1.0 MT
OCT – Simple Process

- Step 1: Purification
- Step 2: Reaction
- Step 3: Recovery

C₄ Feed → Ethylene

Propylene
Ultra-High Purity Propylene >99.9+%

No Superfractionators Required

Energy Neutral Reaction

Guard Bed  OCT Reactor  Ethylene Column  Propylene Column

Ethylene Feed  Recycle Ethylene  Lights Purge

Fixed Bed Reactor

C₄ Feed  C₄ Recycle  C₄ Plus  Propylene Product
Key Reaction Conditions

- Vapor phase equilibrium reaction
- Fixed bed catalyst system
- 70% once-through n-butene conversion
- Typically 85-95% overall n-butene conversion
- Propylene selectivity is greater than 92%
- Nearly isothermal conditions
- “Energy Neutral” reaction
  - Reaction is slightly exothermic so energy is liberated
  - OCT is the only route to propylene which does not require energy input to the reaction
- Metathesis chemistry using Olefins Conversion Technology – OCT – has been licensed in 47 plants, 46 since 2000 using $\text{C}_4$s from
  - Steam crackers
  - Refineries
  - Methanol-to-olefins units
- $\text{C}_5$s from MTO has been incorporated into four ongoing projects
Why Olefins Conversion Technology?

- OCT is a highly efficient process for propylene production
  - Less than 5 - 8% of reaction side products are produced
- Energy-neutral reaction
  - Energy consumption is limited to product recovery
- Lowest capital investment for propylene production
- Ultra-high purity propylene product \(\Rightarrow 99.9+\%\)
50 kta to >750 kta OCT propylene capacity

OCT Commercial Plant Capacities

OCT - Easily Scalable
Case 1 Standalone Ethylene Plant

Steam Cracker

Naphtha

LPG

C\textsubscript{4} Recycle

C\textsubscript{5} Recycle

Fuel Gas

PG Ethylene

PG Propylene

Butadiene

Benzene

C\textsubscript{6} plus

C\textsubscript{4}s

C\textsubscript{5}s

C\textsubscript{6}+
Case 2 Ethylene Plant Integrated with $C_4$ OCU

Steam Cracker

- Naphtha
- LPG
- $C_4$ Recycle
- $C_5$ Recycle

Butadiene Extraction

- $C_4$s

Partial Hydrogenation

- $C_5$s

Hydrogenation/Benzene Recovery

- $C_6^+$

OCU

- Fuel Gas
- PG Ethylene
- PG Propylene
- Butadiene
- PG Propylene
- Benzene
- $C_6$ plus
Case 3 Ethylene Plant Integrated with C₄ - C₅ OCU

Steam Cracker

Butadiene Extraction

OCU

Hydrogenation/Benzene Recovery

Naphtha

LPG

C₄/C₅ Recycle

C₄s

C₅s

C₆+

Fuel Gas

PG Ethylene

PG Propylene

Butadiene

PG Propylene

Benzene

C₆ plus
### Material Balance Comparison

<table>
<thead>
<tr>
<th></th>
<th>Case 1 No OCU</th>
<th>Case 2 C₄ OCU</th>
<th>Case 3 C₄/C₅ OCU</th>
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</thead>
<tbody>
<tr>
<td><strong>Total Olefins</strong></td>
<td>1,582</td>
<td>1,668</td>
<td>1,709</td>
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<td><strong>Propylene to Ethylene</strong></td>
<td>0.58</td>
<td>0.73</td>
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<td><strong>Feeds, kta</strong></td>
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<tr>
<td>Naphtha</td>
<td>2,599</td>
<td>2,668</td>
<td>2,717</td>
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<tr>
<td>LPG</td>
<td>161</td>
<td>165</td>
<td>168</td>
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<tr>
<td>Reaction Water</td>
<td>4</td>
<td>4</td>
<td>4</td>
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<tr>
<td><strong>Total</strong></td>
<td>2,764</td>
<td>2,837</td>
<td>2,889</td>
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<tr>
<td><strong>Products, kta</strong></td>
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<tr>
<td>Methane Rich Offgas</td>
<td>469</td>
<td>459</td>
<td>454</td>
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<tr>
<td>PG Ethylene</td>
<td>1,000</td>
<td>962</td>
<td>935</td>
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<tr>
<td>PG Propylene</td>
<td>582</td>
<td>588</td>
<td>602</td>
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<tr>
<td>PG Propylene from OCU</td>
<td>-</td>
<td>118</td>
<td>172</td>
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<tr>
<td>Butadiene</td>
<td>163</td>
<td>162</td>
<td>164</td>
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<td>Butadiene Vents and Purge</td>
<td>8</td>
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<tr>
<td>Benzene Product</td>
<td>122</td>
<td>125</td>
<td>126</td>
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<tr>
<td>C₆+ Heavies</td>
<td>416</td>
<td>415</td>
<td>424</td>
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<tr>
<td>Acid Gasses</td>
<td>3</td>
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<tr>
<td>Water</td>
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<td>1</td>
<td>1</td>
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<tr>
<td><strong>Total</strong></td>
<td>2,764</td>
<td>2,837</td>
<td>2,889</td>
</tr>
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### Operating Margin Comparison

<table>
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<tr>
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<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>No OCU</td>
<td>C₄ OCU</td>
<td>C₄/₅ OCU</td>
</tr>
<tr>
<td>Feed Cost, MM$/Yr</td>
<td>2,154</td>
<td>2,216</td>
<td>2,252</td>
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<tr>
<td>Product Value, MM$/Yr</td>
<td>3,032</td>
<td>3,160</td>
<td>3,234</td>
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<td>Product Margin, MM US $/Yr</td>
<td>878</td>
<td>944</td>
<td>982</td>
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<tr>
<td>Δ Product Margin, MM US $/Yr</td>
<td></td>
<td>66</td>
<td>104</td>
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<tr>
<td>Energy Cost, MM US $/Yr</td>
<td>146</td>
<td>148</td>
<td>153</td>
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<tr>
<td>Operating Margin, MM US $/Yr</td>
<td>732</td>
<td>796</td>
<td>829</td>
</tr>
<tr>
<td>Δ Operating Margin, MM US $/Yr</td>
<td></td>
<td>64</td>
<td>97</td>
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</table>
Integration of an ethylene plant with OCT increases propylene yield by up to 33% compared to recycle cracking of the $C_4$s and $C_5$s.

Energy consumption per metric ton of ethylene + propylene drops by 5%.

Operating margin improves by 13%.
Dimerization with OCT
Ultimate Flexibility
Ethylene Dimerization Technology to C₄

Exothermic process – no energy input
Olefins Conversion Technology

\[
\text{Ethylene} + \text{Butene-2} \rightarrow 2 \text{Propylene Ethylene}
\]

Energy neutral
## Ethylene to Propylene

<table>
<thead>
<tr>
<th>Product</th>
<th>Value</th>
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<tbody>
<tr>
<td>Ethylene</td>
<td>110.26 kta</td>
</tr>
<tr>
<td>Propylene</td>
<td>100.00 kta</td>
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<tr>
<td>Gasoline Product</td>
<td>6.65 kta</td>
</tr>
<tr>
<td>Heavies Product</td>
<td>0.34 kta</td>
</tr>
<tr>
<td>C(_4)+ Purge</td>
<td>1.11 kta</td>
</tr>
<tr>
<td>OCU Unit Lights</td>
<td>2.16 kta</td>
</tr>
<tr>
<td>Utilities</td>
<td>$24.96 per tonne</td>
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</table>

Net 108 kta ethylene per kta propylene

Low utility needs – mainly LP steam & CW
- **New unit**
  - Dimerization with OCT can be scaled to meet any propylene demand
- Existing OCT unit
  - Dimerization can be installed to make up shortfalls in C<sub>4</sub> feed
  - Raw C<sub>4</sub> can bypass selective hydrogenation and be sent for butadiene extraction with shortfall of butenes being made up by dimerization
  - OCT can be debottlenecked to increase propylene capacity
- Dimerization has no butanes
Propylene from Ethane

Relative TICs for ethane cracker with and without dimerization and OCT

Low cost for large increase in product flexibility

1000 kta ethylene

400 kta propylene & 570 kta ethylene
Propylene from Naphtha

Steam Cracker → OCT
→ Propylene 1.1 to 100%

Raw C4s

Steam Cracker → Dimer

Steam Cracker → OCT
→ Propylene 0.8 to 1.1
Ethylene 1.0

Steam Cracker → OCT
→ Propylene 0.55 to 0.65
Ethylene 1.0

Increasing P/E
### Propylene from Naphtha

<table>
<thead>
<tr>
<th></th>
<th>Naphtha Cracking</th>
<th>Naphtha w/OCT</th>
<th>Naphtha w/Dimer &amp; OCT</th>
<th>Naphtha w/Dimer &amp; OCT</th>
<th>Naphtha w/Dimer &amp; OCT</th>
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</thead>
<tbody>
<tr>
<td>Naphtha Feed</td>
<td>3328</td>
<td>3328</td>
<td>3328</td>
<td>3328</td>
<td>3328</td>
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<tr>
<td>Net Ethylene</td>
<td>1100</td>
<td>998</td>
<td>806</td>
<td>400</td>
<td>0</td>
</tr>
<tr>
<td>Propylene</td>
<td>602</td>
<td>920</td>
<td>1100</td>
<td>1487</td>
<td>1867</td>
</tr>
<tr>
<td>Gasoline/FO</td>
<td>613</td>
<td>620</td>
<td>624</td>
<td>633</td>
<td>642</td>
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<tr>
<td>P/E Ratio</td>
<td>0.55</td>
<td>0.92</td>
<td>1.37</td>
<td>3.72</td>
<td></td>
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<tr>
<td>Total E&amp;P</td>
<td>1702</td>
<td>1918</td>
<td>1906</td>
<td>1886</td>
<td>1867</td>
</tr>
</tbody>
</table>

**Complete control of P/E ratio**
Propylene from Naphtha

Relative TIC

Naptha total propylene
- 0 Ethylene/1867 Propylene

Naphtha w/dimer/OCT
- 400 Ethylene/1487 Propylene

Naphtha w/dimer/OCT
- 806 Ethylene/1100 Propylene

Naphtha w/OCT
- 998 Ethylene/920 Propylene

Naphtha Cracker
- 1100 Ethylene/602 Propylene

Small additional cost for total propylene flexibility
Propylene to Ethylene Price

- North America P/E price about 1
- Middle East and Asia-Pacific Propylene price above Ethylene price

Source: GlobalData
Maximizing Profits under Volatile Pricing

Flexibility with Olefin Production as $f$(Propylene to Ethylene Price)

In a dynamic market, a low cost, flexible dimerization and OCT will allow you to make the most profitable olefin.

Source: GlobalData
Metathesis chemistry has played a major role in on-purpose propylene production accounting for about 10% of the world’s propylene.

Expanding the feed slate from C₄s to C₅s improves both ethylene plant and refinery operating margins.

OCT integrated with dimerization unit provides complete flexibility in ethylene and propylene production during volatile pricing.

Energy consumption and greenhouse gas emissions are reduced.

Simple payout times of 2 years to 2.5 years.
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