C₅ Olefins Conversion – Improving Refinery and Steam Cracker Economics

Robert Haines

CB&I

Polymer-Grade Propylene from FCC and Cracker based C₅s

World Petrochemical Conference

Petrochemical Technology Renaissance Seminar

Houston, Texas - March 27-28, 2014
- 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 C₃ and heavier products opening up the need for greater by-product flexibility in both new and existing plants
- 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

Olefins conversion has and will continue to play a key role in on-purpose propylene production
OCT is a highly efficient and selective process for propylene production
- Takes C_4 or C_5 olefins and ethylene $\Rightarrow$ propylene
- Less than 2% of undesirable side products are produced

Energy-neutral reaction
- Energy consumption is limited to product recovery
- Lowest greenhouse gas production

Lowest capital investment for propylene production
- Simple process, moderate conditions
- No superfractionators

Ultra-high purity propylene product $\Rightarrow$ 99.9+%
- OCT for improved alkylation quality
  - Process makes isobutene as a byproduct which is a high value alkylation feedstock
- OCT for improvement in gasoline RVP
- OCT for higher quality products
  - $C_4$ and $C_5$ hydrocarbons go to propylene, not gasoline or recycle cracking
- OCT for product flexibility
  - Steam cracker can shift from ethylene mode to propylene mode (with dimerization of ethylene)
  - Refinery can shift from gasoline to propylene
- OCT for greenhouse gas reduction
- Increase refinery operating margins up to 20%
- Increase steam cracker margins up to 13%
C₄s and C₅s as OCT Feedstock

Crude Fractions

Methanol-to-Olefins
By-product

FCC Recovery

Steam Cracker
Pyrolysis Gasoline
(Main Reaction)

N-Butene + Ethylene
1.00 ton  0.50 ton

2 Propylene
1.50 ton

Energy neutral

Low greenhouse gas emissions
Net C$_5$ OCT Chemistry

i+n Pentenes 1.00 ton  +  Ethylene 0.54 ton  →  Propylene 1.17 ton  +  Isobutene 0.37 ton

Energy neutral

Low greenhouse gas emissions

Tonnage rates based on typical refinery mix of i+n pentenes
Lower yield from cracking

<table>
<thead>
<tr>
<th>FEED</th>
<th>$C_4s$</th>
<th>$C_5s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield</td>
<td>$C_2^- + C_3^-$</td>
<td>$C_2^- + C_3^-$</td>
</tr>
<tr>
<td>Cracking</td>
<td>35%</td>
<td>27%</td>
</tr>
<tr>
<td>Metathesis</td>
<td>70%</td>
<td>63%</td>
</tr>
</tbody>
</table>

Lower energy requirement for metathesis
- The metathesis reaction is energy neutral and by products are easily fractionated

<table>
<thead>
<tr>
<th>Specific Energy</th>
<th>Kcal/Kg $C_2^- + C_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cracking</td>
<td>4,500</td>
</tr>
<tr>
<td>Metathesis</td>
<td>2,000</td>
</tr>
</tbody>
</table>

Better yield and lower energy with metathesis than from recycle cracking
Decreasing RVP specification for gasoline means less C₅s can be blended into the gasoline pool

Upgrading the C₅s to propylene adds to product value

$67 \text{ MM per year for a 68,000 BPD FCC}$
Olefins Conversion Technology – OCT – has been used in 46 plants since 2000 using C₄s and C₅s
  - Steam cracker
  - Refineries
  - Methanol-to-olefins units

Total production of 8400 KTA
  - >10% of world capacity

C₅s from MTO has been incorporated into four ongoing projects
- Low pressure recovery (for ethylene)
  - Impurity removal (wash, reaction, adsorption)
  - Ethylene recovery (chilling and patented recovery technique)
OCT – a Simple Three Step Process

- **Step 1**
  - Purification

- **Step 2**
  - Reaction

- **Step 3**
  - Recovery

C\textsubscript{4} C\textsubscript{5} Feed → Ethylene → Propylene
- Steam cracker C\textsubscript{4} and C\textsubscript{5} feed to OCT
- FCC C\textsubscript{4} and FCC C\textsubscript{5} feed to OCT
  - with and without low pressure recovery of ethylene (LPR)
- Ultimate product flexibility with addition of ethylene dimerization
Stand-alone Ethylene Plant

Steam Cracker

- Naphtha
- LPG
- C₄ Recycle
- C₅ Recycle

Partial Hydrogenation
- C₄ᵣ
- C₅ᵣ
- C₆⁺

Butadiene Extraction
- Butadiene

Hydrogenation/Benzene Recovery
- Benzene
- C₆ plus

Fuel Gas
- PG Ethylene
- PG Propylene
Ethylene Plant Integrated with $C_4 - C_5$ OCU

- Naphtha
- LPG
- $C_4/C_5$ Recycle
- $C_4$s
- $C_5$s
- $C_6+$

Steam Cracker

Butadiene Extraction

OCU

Fuel Gas
PG Ethylene
PG Propylene
Butadiene
PG Propylene
Benzene
$C_6$ plus
### Ethylene Plant OCT Integration – 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>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total Olefins</strong></td>
<td>1,582</td>
<td>1,668</td>
<td>1,709</td>
</tr>
<tr>
<td><strong>Propylene to Ethylene</strong></td>
<td>0.58</td>
<td>0.73</td>
<td>0.83</td>
</tr>
<tr>
<td><strong>Feeds, kta</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphtha</td>
<td>2,599</td>
<td>2,668</td>
<td>2,717</td>
</tr>
<tr>
<td>LPG</td>
<td>161</td>
<td>165</td>
<td>168</td>
</tr>
<tr>
<td>Reaction Water</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>2,764</td>
<td>2,837</td>
<td>2,889</td>
</tr>
<tr>
<td><strong>Products, kta</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane Rich Offgas</td>
<td>469</td>
<td>459</td>
<td>454</td>
</tr>
<tr>
<td>PG Ethylene</td>
<td>1,000</td>
<td>962</td>
<td>935</td>
</tr>
<tr>
<td>PG Propylene</td>
<td>582</td>
<td>588</td>
<td>602</td>
</tr>
<tr>
<td>PG Propylene from OCU</td>
<td>-</td>
<td>118</td>
<td>172</td>
</tr>
<tr>
<td>Butadiene</td>
<td>163</td>
<td>162</td>
<td>164</td>
</tr>
<tr>
<td>Butadiene Vents and Purge</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Benzene Product</td>
<td>122</td>
<td>125</td>
<td>126</td>
</tr>
<tr>
<td>C₆+ Heavies</td>
<td>416</td>
<td>415</td>
<td>424</td>
</tr>
<tr>
<td>Acid Gasses</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Water</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>2,764</td>
<td>2,837</td>
<td>2,889</td>
</tr>
</tbody>
</table>

Higher naphtha feed rates produce the same furnace effluent as Case 1.
Ethylene Plant OCT Integration – Operating Margin Comparison

<table>
<thead>
<tr>
<th></th>
<th>No OCU</th>
<th>C₄ OCU</th>
<th>C₄/C₅ OCU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Cost, MM$/Yr</td>
<td>2,154</td>
<td>2,216</td>
<td>2,252</td>
</tr>
<tr>
<td>Product Value, MM$/Yr</td>
<td>3,032</td>
<td>3,160</td>
<td>3,234</td>
</tr>
<tr>
<td>Product Margin, MM US$/Yr</td>
<td>878</td>
<td>944</td>
<td>982</td>
</tr>
<tr>
<td>Δ Product Margin, MM US$/Yr</td>
<td></td>
<td>66</td>
<td>104</td>
</tr>
<tr>
<td>Energy Cost, MM US$/Yr</td>
<td>146</td>
<td>148</td>
<td>153</td>
</tr>
<tr>
<td>Operating Margin, MM US$/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>
</tr>
</tbody>
</table>

- Integration of an ethylene plant with OCT increases propylene yield by up to 33% compared to recycle cracking of the C₄s and C₅s
- Energy consumption per metric ton of ethylene + propylene drops by 5%

**Operating margin improves by 13%**
Refinery Integration – Gasoline Routing

Crude

CDU and VDU

Heavy Naphtha

NHT and Reformer with Aromatics Extraction

Benzene

C7+ Reformate

C4s to Alkylation

Alky Unit

Gasoline Pool

FCC C4

FCC C5

FCC with Gas Plant Gasoline Splitter and Treating

C6+ to Gasoline

To Coking
Refinery Integration – Gasoline Routing

Heavy Naphtha

NHT and Reformer with Aromatics Extraction

C₄s to Alkylation

Alky Unit

C₇+ Reformate

Gasoline Pool

Crude

CDU and VDU

To Coking

All units can integrate with LPR – reduces ethylene import

FCC C₄

OCU

C₅ rich to Gasoline

Ethylene

FCC C₅

LPR

C₆⁺ to Gasoline

CDU and VDU

Calculation: 

FCC C₄

OCU

C₅ rich to Gasoline

Ethylene

FCC C₅

LPR

C₆⁺ to Gasoline

CDU and VDU

Calculation: 

FCC C₄
# Summary Refinery Cases – Margins and Payout

<table>
<thead>
<tr>
<th></th>
<th>Base</th>
<th>$C_5$ OCU</th>
<th>$C_5$ OCU W/LPR</th>
<th>$C_4C_5$ OCU</th>
<th>$C_4C_5$ with LPR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene Production, (kMTA)</td>
<td>-</td>
<td>165</td>
<td>165</td>
<td>290</td>
<td>290</td>
</tr>
<tr>
<td>Gasoline Prod, (BBL/Day)</td>
<td>68,900</td>
<td>68,100 (-1%)</td>
<td>68,100 (-1%)</td>
<td>63,500 (-8%)</td>
<td>63,500 (-8%)</td>
</tr>
<tr>
<td>Ethylene Import, (kMTA)</td>
<td>-</td>
<td>82</td>
<td>51</td>
<td>124</td>
<td>93</td>
</tr>
<tr>
<td>Gross Margin, ($MM/yr)</td>
<td>500</td>
<td>567</td>
<td>603</td>
<td>580</td>
<td>617</td>
</tr>
<tr>
<td>Gross Margin Improvement, ($MM/yr)</td>
<td>-</td>
<td>67</td>
<td>103</td>
<td>80</td>
<td>117</td>
</tr>
<tr>
<td>Net Margin Improvement, ($ MM/yr)</td>
<td>-</td>
<td>58</td>
<td>84.4</td>
<td>73</td>
<td>100</td>
</tr>
<tr>
<td>Total Installed (ISBL) Cost, ($MM)</td>
<td>-</td>
<td>83</td>
<td>148</td>
<td>133</td>
<td>197</td>
</tr>
<tr>
<td>Simple Payout, (Yrs)</td>
<td>1.4</td>
<td>1.8</td>
<td>1.8</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

**12-20% margin increase**

All cases have less than two year simple payback

$C_4C_5$ cases have 75% more propylene and larger impact on gasoline production

Addition of LPR can reduce imported ethylene up to 38% (based on typical FCC)
Dimerization with OCT
Ultimate Flexibility
Ethylene Dimerization Technology to $C_4$

Exothermic process – no energy input
## Ethylene to Propylene

<table>
<thead>
<tr>
<th>Product</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>110.26</td>
<td>kta</td>
</tr>
<tr>
<td>Propylene</td>
<td>100.00</td>
<td>kta</td>
</tr>
<tr>
<td>Gasoline Product</td>
<td>6.65</td>
<td>kta</td>
</tr>
<tr>
<td>Heavies Product</td>
<td>0.34</td>
<td>kta</td>
</tr>
<tr>
<td>$C_4+$ Purge</td>
<td>1.11</td>
<td>kta</td>
</tr>
<tr>
<td>OCU Unit Lights</td>
<td>2.16</td>
<td>kta</td>
</tr>
<tr>
<td>Utilities</td>
<td>$24.96</td>
<td>per tonne</td>
</tr>
</tbody>
</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
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
Maximizing Profits under Volatile Pricing

Flexibility with Olefin Production as $f(\text{Propylene to Ethylene Price})$

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

Source: GlobalData

---

North America, 2000-2016
- Convert ethylene to propylene
- Sell ethylene

Middle East, 2000-2016
- Convert ethylene to propylene
- Sell ethylene

Asia-Pacific, 2000-2016
- Convert ethylene to propylene
- Sell ethylene
Metathesis chemistry has played a major role in on-purpose propylene production producing about 10% of the world’s propylene.

Adding olefins conversion of C₅ improves refinery and cracker operating margins:
- Minimum $67 MM/yr product improvement for a 68,000 BPD FCC unit
  - Up to 20% net margin improvement when combined with LPR and C₄
  - 13% net margin improvement over recycle cracking for a 1000 KTA Cracker

Improved gasoline quality (reduced RVP/isobutene by-product)

OCT/Dimer provides flexibility in cracker product slate with volatile market

Energy consumption and greenhouse gas emissions are reduced

Simple payout times of 2 years to 2.5 years result

MTO sourced C₅s in commercial design. Startup in 2015.
Refinery and cracker C₅s fully developed and ready for commercialization
Technology
- Licensed technology
- Engineering/technical services
- Proprietary catalysts
- Specialty equipment
- Consulting services

Fabrication Services
- Modularization
- Fabrication
- Erection
- Engineering

Engineering, Construction and Maintenance
- Engineering
- Procurement
- Module fabrication
- Construction
- Commissioning

Government Solutions
- Program and project management
- Engineering, procurement and construction
- Environmental engineering and consulting
- Emergency response and recovery
- Environmental remediation
"This paper and Program may contain confidential or proprietary information. The information, observations, and data presented in this paper and Program are intended for educational purposes only and do not identify, analyze, evaluate, or apply to actual, specific engineering or operating designs, applications, or processes. The comments and opinions are based on available information, and in all cases reference shall be made to the actual wording and meaning of applicable codes and standards. The use of or reliance on any information, observations, or data provided is solely at your own risk."
THANK YOU!