Light Olefin Technologies

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Alternatives to Thermal Cracking for the production of light olefins:

- Propane dehydrogenation to Propylene
  - Oleflex process

- Olefin Conversion Processes
  - Metathesis
  - Olefin Cracking

- Methanol to Olefins
  - SAPO-34 and ZSM-5 based systems

- High Severity FCC processes
  - PetroFCC

- Naphtha cracker feed enrichment
  - MaxEne Process for separation of normal paraffins from naphtha for increased naphtha cracker ethylene yield
Issues to Consider

- Feed availability and price
- Relative Capex
- Multi product slate / integration
Propane Dehydrogenation

- On-purpose production of propylene from propane
- Produces propylene and hydrogen
- Typically Pt or Cr based systems

Propane: $C_3H_8$

Catalyst

Propylene & Hydrogen: $C_3H_6$ & $H_2$
Propane Dehydrogenation
The Oleflex Process

1.2 MT Propane

VC + FC Inputs

Utilities
Catalyst
Chemicals
Labor, etc.

High yield Pt based catalyst

1.0 MT Propylene
Propane Dehydrogenation
The Oleflex Process

Net Gas → Oleflex → SHP → Deethanizer
H₂ → Oleflex → SHP → Propylene
C₃ LPG → Depropanizer → C₄+
C₂⁻ → P-P Splitter
Propane Dehydrogenation
The Oleflex Process

Reactors Section

Heater Cells

Regeneration Section

Separator

Off Gas

To SHP

Dryer

Turbo Expander

Rx Effluent

Compressor

Regeneration Section

Product Recovery Section

H₂ Recycle

Fresh & Recycle Feed

Net Separator Off Gas

H₂ Recycle

To SHP
Olefin Conversion Processes

Two types: Metathesis & Olefin Cracking

Catalyst

Ethylene & 2-Butene

C₂H₄ & C₄H₈

Catalyst

Metathesis

Propylene

C₃H₆

(plus by-products)

C₄ to C₈ Olefins

C₄H₈ to C₈H₁₆

Catalyst

Olefin Cracking

- ΔT

Ethylene & Propylene

C₂H₄ & C₃H₆

(plus by-products)
Olefin Cracking
TOTAL PETROCHEMICALS / UOP Olefin Cracking Process

Olefinic
C₄ - C₈
Feed

SHP

Olefinic
C₄ & C₅
Depropanizer
Column

Light
Olefin
Product

C₆+
Purge

Rerun
Column

Recycle

OC
Reactor

C₄ & C₅
Purge

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• \( \text{C}_4 \) do not crack directly

• In principle, it is possible to produce Propylene and higher olefins from Ethylene
  
  - Ethylene activation is facilitated in the presence of higher olefin
• 80% to 90% overall conversion of higher olefins
• High selectivity to light olefins
  - 3.5 to 4.0 propylene/ethylene product ratio
• Over 90% olefin purity in C₂ & C₃ fractions
  - Upgrading to polymer grade is simple
• Fixed-bed technology
  - Swing regeneration system
  - High LHSV
  - Low Rx pressure (between 1 and 5 bar)
• Reactor inlet temperatures 500 to 600°C
• No diluent addition
Olefin Cracking can be integrated with a variety of other processes

Naphtha Crackers

- Furnace
- Olefin Cracking
- Product Recovery & Purification
- Light Olefins
- Gas Oils
- C_{4}/C_{5}
- C_{5}/C_{6} Paraffin-Rich

Refineries

- FCC
- Gasoline Cycle Oils
- Light Olefins
- C_{2}=
- C_{3}=
- C_{4}=
- LPG

MTO Plants

- MTO
- MeOH
- Light Olefins
- C_{2}=
- C_{3}=
- C_{4}+

- Olefin Cracking
- C_{4}-C_{5} Olefins
- Paraffin-Rich

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Methanol to Olefins

Gas to Olefins (GTO)

Natural Gas

- Synthesis Gas Production
- Methanol Synthesis

MTO

Ethylene & Propylene

Coal

Coal to Olefins (CTO)
Methanol to Olefins
ZSM-5

ZSM-5 (MFI)

- Mobil discovered ZSM-5 for methanol to gasoline (MTG) and olefins during early 1970s
- MTG commercialized in New Zealand during mid 1980s.

Medium pore size: 5.1 x 5.5Å
**SAPO-34**

- **Silicoalumino-Phosphates (SAPO)** discovered in the early 1980s by scientists at Union Carbide (UCC)
- SAPO-34 has high selectivity for MTO reaction.
- MTO development transferred from UCC to UOP in 1988

Methanol to Olefins
SAPO-34 Comparison to ZSM-5

Small Pore Weak Acid Sites

Medium Pore Strong Acid Sites

SAPO-34

ZSM-5

3.8 Å

5.5 Å

Ethylene

Propylene

Isobutylene

Benzene
Methanol to Olefins
Once Through Yields SAPO-34 and ZSM-5

- SAPO-34 produces more light olefins
- SAPO-34 has slightly higher coke selectivity
- \( C_4^+ \) olefin conversion could improve light olefin yields

<table>
<thead>
<tr>
<th></th>
<th>SAPO-34 Type</th>
<th>ZSM-5 Type</th>
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</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>31</td>
<td>6</td>
</tr>
<tr>
<td>Propylene</td>
<td>47</td>
<td>42</td>
</tr>
<tr>
<td>Light Olefins</td>
<td>78</td>
<td>48</td>
</tr>
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</table>
Methanol to Olefins
Yields with $C_4^+$ Olefin Recycle

<table>
<thead>
<tr>
<th>Type</th>
<th>SAPO-34</th>
<th>ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>29</td>
<td>nil</td>
</tr>
<tr>
<td>Propylene</td>
<td>60</td>
<td>65</td>
</tr>
<tr>
<td>Light Olefins</td>
<td>89</td>
<td>65</td>
</tr>
<tr>
<td>MeOH Consumption, kg/kg Olefin</td>
<td>2.6</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Low methanol consumption

- $C_4^+$ from SAPO almost entirely converted
- $C_4^+$ from ZSM-5 higher in aromatics
Methanol to Olefins
UOP/HYDRO MTO Process

- Fluidized bed reactor & regenerator with continuous steady state operation and polymer-grade ethylene and propylene product
• Heavies can be converted using UOP/Total Petrochemicals Olefin Cracking Process (OCP)
• Zeolite based system is needed for heavies conversion – higher acidity, larger pore size.
• Increased propylene production thanks to:
  - Catalyst improvements
  - Process optimization

P/E up to 2.1 with high selectivity
FCC Unit Design & Operating Envelopes

Propylene Yield, wt-

Gasoline + LPG

Maximum Gasoline

Maximum Propylene

Gasoline Yield, wt-

f (Rx T, P_p, C/O, P_T)

PetroFCC Technology
The PetroFCC™ Process

- Ethylene
- Propylene
- Mixed C₄s
- Aromatic naphtha
- Cycle oils

- High cat / oil
  - **RxCat technology:**
  - De-couples catalyst circulation from heat balance

- Low partial pressure
  - Optimize Steam and Operating Pressure

- Optimized Catalyst Selection
- High Temperature
- Increased flexibility
Naphtha Cracker Feed Enrichment
The MaxEne Process

- Adsorptive separation system for extraction of normal paraffins from naphtha
  - Full range naphtha (C₆ to C₁₂)
  - Extract
    - High recovery of normal paraffins
    - Normal paraffin purity up to 95%
    - Liquid phase, low temperature and pressure
    - Low utilities
  - Raffinate
    - Superior catalytic reformer feed
Naphtha Cracker Feed Enrichment
The MaxEne Process

Adsorptive separation
- The adsorbent has greater affinity for \( n \)-paraffins

Simulates a moving bed
- The process influent and effluent points move, but the actual mechanical connections do not
- The solid adsorbent is in packed, non-moving beds
- The liquid feed flows counter-currently relative to the solid

Diagram:
- Adsorptive chamber
- Rotary valve
- Extract column
- Raffinate column
- Pumparound pump
- Naphtha
- Paraffin feed to steam cracker
- Desorbent feed to reformer
The MaxEne Process Effect
Single-pass Steam Cracker Yields

Cracker effluent, wt-%

<table>
<thead>
<tr>
<th>Compound</th>
<th>Typical Complex</th>
<th>With a MaxEne Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>Methane</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>Ethane</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Propene</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Ethane</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Propylene</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Butylene</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Pygas</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

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Conclusions

- New routes must be considered to meet future ethylene and propylene demand
- A range of economically attractive options are available to meet this demand
- Each producer must consider key selection factors
  - Feedstock availability
  - Desired product slate
  - Integration with existing facilities
Q & A