Increasing Petrochemicals Project Earnings by Upgrading Steam Cracker C4s and C5s

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Today’s presentation will cover C4s and C5s processing routes, including:

- Butadiene Extraction
- Metathesis to produce Propylene from both C4s and C5s Olefins
- Skeletal Isomerization to convert either normal or iso C4s and C5s
- Linear and Skeletal Isomerization for increased Butene 1 production
- Metathesis and Isomerization to produce Butene 1 and Hexene 1
- Etherification to produce MTBE or TAME
Maximize butadiene yield for highest operating margin

Butadiene prices higher than ethylene and propylene

Source ICIS Pricing
Process Overview – Butadiene Extraction

**Extractive Distillation**
- **C₄ Feed**
- **Degassed NMP**
- **C₄ S + NMP**
- **C₄ Vapor**

**Crude Butadiene**

**Distillation**
- **Raffinate**
- **Propyne**
- **1,3 Butadiene Product**
- **1,2 Butadiene**

**Solvent Degassing**
- **C₄ Acetylenes**
Butadiene Extraction Market Leadership

- Leading (first quartile) technology in butadiene extraction
- Best solvent: NMP
  - Lowest environmental impact, non-corrosive, highest selectivity
- Lowest fouling system
  - Operating periods over five years between shutdowns
  - Average on-stream factor 8300-8500 hours per year
  - Incorporates “popcorn prevention” system
- Commercially proven with 33 operating plants
- Capacities from 65 to 900 MMlb/y
- Commitment to technology improvement
- Ongoing technical support from Lummus and BASF
The Solvents: Eco-Efficiency Analysis

NMP has lowest environmental impact and cost

NMP is less in all categories

NMP is the best solvent for butadiene extraction

- NMP process
- DMF process
- ACN process
Methathesis Chemistry for Improved Operating Margin

- Steam cracker & refinery C4’s & C5’s can be upgraded using metathesis chemistry
- Olefins Conversion Technology (OCT) is the only commercially demonstrated metathesis technology
- Since 2000, Lummus Technology has licensed 37 plants based on the OCT process
  - Over 8 million tons of capacity
  - More than 10% of world’s propylene capacity
- Benefits include:
  - Upgrade of C4’s & C5’s to high value propylene
  - Low CO₂ production
  - Low utility consumption
  - Low capital investment
  - Quick project turnarounds
Propylene Selectivity Comparison

% Propylene Yield

“By-product” Technologies

“On-purpose” Technologies

Ethane  Naphtha  FCC  MTO  PDH  OCT
Olefins Conversion Technology Economics

Relative Investment

Traditional OCT feed sources: Steam cracker and FCC

OCT is low cost on-purpose propylene production option

Ref: CMAI
Ethylene  Butene Metathesis

Main Metathesis Reaction

\[
\text{1 mole Butene-2} + \text{1 mole Ethylene} = \text{2 moles Propylene}
\]

OCT upgrades lower cost butenes
0.74 ton C₄ \(\rightarrow\) 1 ton propylene
Ethylene/Pentene Metathesis

Main Metathesis Reaction

Ethylene + Propylene + Butene-1 → Pentene-2
Value added by OCT

Butenes 0.74 ton  Ethylene 0.31 ton  Propylene 1.00 ton
$550/ton  $1100/ton  $1100/ton

Catalyst + Utilities  $30/ton

$350/ton upgrade

> $52 million/year for a 150 kta OCT
Ethylene/Pentene OCT

- Steam cracker C₅s typically hydrogenated to olefins or paraffins and recycled to cracking heaters
- After selective hydrogenation, C₅s can now be fed to OCT as additional feedstock

*Ethylene + propylene yield increases by 2.5 times compared to cracking*
Improved Margins – C$_4$/C$_5$ OCT

Value Added to C4 only OCT

Expected payback less than 2 years
OCT Process Scheme a Simple Process

Ultra-high purity propylene >99.9+%  

Guard Bed  OCT Reactor  Ethylene Column  Propylene Column

Ethylene Feed  Recycle Ethylene  Lights Purge

Fixed bed reactor

C₄ & C₅ Feed  C₄ & C₅ Recycle  C₄ Plus

No superfractionators required

Energy-neutral reaction
CD/Isis Process

• CD/Isis isomerizes both isobutene & isopentene to normal butene & pentene to increase OCU feed
• CD/Isis unit, integrated with OCT, is an effective way of converting low-value isobutene & isopentene to ultimately high-value propylene product
Chemistry

- Chemistry:
  - Olefin skeletal isomerization
  - Equilibrium reaction
    - Can go both ways
    - Temperature sets equilibrium distribution

Isobutene $\rightleftharpoons$ Butene-1 $\rightleftharpoons$ Butene-2
**CD/Isis SM** Skeletal Isomerization of Isobutene

**Conventional Processing**

- Mixed $\text{C}_4$s Olefins
- CDs
- Conventional Processing
  - CD-DelB
  - OCT
  - Poor Cracking selectivity
  - Isobutene/
    - Isobutane to
    - Cracking
  - Ethylene
  - Propylene

**CD/Isis Unit for more Propylene**

- Mixed $\text{C}_4$s Olefins
- CDs
  - CD-DelB
  - OCT
  - CDIsis
  - Isobutane
  - Isobutene
- Ethylene
- Propylene

**Adds up to 60% more propylene production**
CD/Isis Unit Integrated with OCT

- **C₄ Treating and Selective Hydrogenation**
  - 255 kta Mixed C₄s
  - 78 kta Isobutane/Isobutene purge
  - H₂

- **CD-DelB Unit**

- **OCT Unit**
  - 34 kta Ethylene
  - 100 kta Propylene Product
  - 43 kta C₄+ By-product
CD/Isis Unit Integrated with OCT

- **Same C₄ feed**: 255 kta Mixed C₄s
- **C₄ Treating and Selective Hydrogenation**: 255 kta Mixed C₄s → CD-DelB Unit
- **CD-DelB Unit**: H₂, i-C₄s
- **CD/Isis Unit**: 78 kta Isobutane/Isobutene purge
- **Fractionator Bottoms Product**: Up to 60% more C₃-
- **OCT Unit**: 54 kta Ethylene
- **OCT Unit**: 160 kta Propylene Product
- **Up to 60% more C₃-**: 160 kta Propylene Product
- **49 kta C₄+ By-product**: 49 kta C₄+ By-product

- **~50% more butenes**: ~50% more butenes
Improved Margins

OCT Integrated with CDIsis Unit

- Gross Margin: $38
- Net Margin: $25

Expected payback less than 2 years
CD/Isis/OCT Integration – Summary

- CD/Isis process is commercially proven
- Simple process, flowsheet and reactor operation similar to OCT unit
- CD/Isis unit integration would increase the net margin by about US$25 million for unit expanded from 100 to 160 kta
- Pay-out in less than 2 years
CPT Chemistry for 1-Butene

- Isomerization technology for 1-Butene

Isomerization

2-Butene \[\rightarrow\] 1-Butene

- Equilibrium conversion \(~20\%\)
- No side reactions
- Energy neutral
CPT Butene Isomerization

- Proven C4 feed treatment system to insure isom catalyst performance
- Maximized heat interchange for low energy input reaction system
- Simple reactor design
- Spare reactors for continuous operation
- Regeneration system included for catalysts and adsorbents
- Proven energy-efficient Sulzer heat pump recovery system (Butene fractionation)
Isobutylene must be removed to meet specification.

Butene content sets recycle and fractionation energy.

CPT Butene Isomerization Process Flow Diagram

Raffinate-2

Butene Fractionator

Feed Pump

Reflex Pump

Product Pump

Sulzer Heat Pump Fractionation System

Raffinate-3

Isomerization Treater

Fuel

Isomerization Reactor

1-Butene

To LPG storage

CPT Butene Isomerization Process Flow Diagram
Ethers Process Chemistry

MTBE

\[
\text{CH}_3\text{C} = \text{CH}_2 + \text{CH}_3\text{-OH} \xrightleftharpoons{} \text{CH}_3\text{C} = \text{CH}_2 + \text{CH}_3\text{OCH}_3
\]

\[\Delta H_r = -8.5 - 9.5\text{ Kcal/mol}\]

ETBE

\[
\text{CH}_3\text{C} = \text{CH}_2 + \text{C}_2\text{H}_5\text{-OH} \xrightleftharpoons{} \text{CH}_3\text{C} = \text{CH}_2 + \text{C}_2\text{H}_5\text{OCH}_3
\]

\[\Delta H_r = -8.5 - 9.5\text{ Kcal/mol}\]
Achieving Very High Conversion

Conventional System

- Reaction followed by separation of product
- followed by reaction followed by another separation
- .......
- More separation steps increase capital cost
- Very high conversion cannot be achieved economically
What is Catalytic Distillation?

Process Simplification by...
Combining reaction and distillation in one single operation
Achieving Very High Conversion

CD System

- Very high conversion can be achieved economically
Catalytic Distillation

CD Modules

Similar to Structured Packing
Contains Catalyst Inside the Packing
Typical CDMtbe Scheme

Primary Reactor  Catalytic Distillation  Methanol Extraction  Methanol Recovery

$C_4$ Feed  $C_4$ Methanol  $C_4$ Raffinate

Methanol

$C_4$ Methanol

Water

MTBE
Conclusion

• Upgrading both steam cracker & refinery C₄’s and C₅’s can enhance profitability
  • Butadiene Extraction
  • OCT
  • CPT
  • MTBE/ETBE
• Lummus supplies all technologies and can therefore optimize upgrading the C4’s and C5’s

Increased Project Earning will result