OLEFINS PRODUCTION

Olefins by steam cracking
Importance of ethylene and propylene in the chemical industry
History
Characteristics of steam cracking
Raw materials and products
Steam cracking processes, steam cracking at TVK
Safety aspects
Control systems
Key equipment
Overview of investment and operating costs
Importance of ethylene and propylene in the chemical industry
Lower olefins: ethylene and propylene

- The largest volume petrochemicals produced
- Annual global production of ethylene in 2010 is about 120 million tons with a continuous annual increase of some 4 - 5 %
- Ethylene and propylene have no end use, they are building blocks for a large variety of chemicals and petrochemical products
- Polymers are the dominating end-users
Building block for petrochemicals – ethylene consumption 2009

- **PE**: 61%
- **Ethylene oxide**: 14%
- **EDC (PVC)**: 12%
- **Styrene**: 6%
- **VAM**: 1%
- **Others**: 6%
Building block for petrochemicals – propylene consumption 2009

- PP: 64%
- Acrylonitrile: 7%
- Propylene oxide: 7%
- Cumene: 5%
- Acrilic acid: 4%
- Isopropanol: 2%
- Others: 11%
Main drivers for ethylene and propylene demand: PE and PP
Global consumption of ethylene and propylene
Hungary: ethylene produced by TVK only

RAW MATERIALS FROM MOL
(NAPHTHA, LPG AND GAS OIL)

OLEFIN-1
370 kt/yr

OLEFIN-2
290 kt/yr

ETHYLENE TO BORSODCHEM

LDPE-2
65 kt/yr

HDPE-1
200 kt/yr

HDPE-2
220 kt/yr

PP-3
100 kt/yr

PP-4
180 kt/yr

CUSTOMERS

CUSTOMERS

CUSTOMERS

PROPYLENE TO SPC

BY-PRODUCTS TO MOL
(ISOBUTYLYLENE, BT CUT, C8 AND C9 CUT)

FUEL OIL TO CARBON BLACK PRODUCER

(POLYETHYLENE, PVC, LDPE, LLDPE, HDPE, PP, OLEFIN, ETHYLENE, PROPYLENE, PETROCHEMICALS, ORTHOXylene, NAPHTHA, LPG AND GAS OIL)
History
Ethylene milestones

- 1913: Standard Oil’s scientist patented thermal cracking process
- 1930ties: Ethylene was first separated from coke oven gas and the first commercial plant for the production of ethylene was built by Linde at that time
- 1941: Standard Jersey (ExxonMobil’s predecessor) developed the world’s first steam cracker at Baton Rouge
- 1950ties: Ethylene emerged as a large-volume intermediate, replacing acetylene as prime material for synthesis

Today ethylene is primarily produced by thermal cracking of hydrocarbons in the presence of steam. Plant capacities are up to 1-1.5 million t/yr ethylene.

Other processes are also available or under development
Olefin production by processes, 2008

- Ethylene production
  - Steam cracking
  - Refinery operation
  - Others

- Propylene production
  - Steam cracking
  - Refinery operation
  - Others
Ethylene at TVK

1975: First steam cracker with Linde process started operation
   - Original nameplate capacity: 250 kt/yr ethylene
   - After several debottlenecking nowadays the actual capacity is 370 kt/yr

2004: Second cracker (also Linde process) with 250 kt/yr capacity was commissioned
   - Today the capacity is 290 kt/yr
Present and future processes to ethylene and propylene production

<table>
<thead>
<tr>
<th>Process</th>
<th>Status</th>
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<tbody>
<tr>
<td>Steam cracking</td>
<td>dominating technology</td>
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<tr>
<td>Refinery processes</td>
<td>minor importance for ethylene</td>
</tr>
<tr>
<td></td>
<td>important for propylene only</td>
</tr>
<tr>
<td>MTO Methanol to Ethylene and Propylene</td>
<td>technology is ready but not yet commercialized</td>
</tr>
<tr>
<td>MTP Methanol selectively to Propylene</td>
<td>commercialisation phase</td>
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<tr>
<td>Syngas via Fisher Tropsch</td>
<td>minor importance</td>
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<tr>
<td>Green Ethylene</td>
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<tr>
<td>- Biomass via Fermentation to Ethanol</td>
<td>commercialisation phase</td>
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<tr>
<td>and Dehydration of Ethanol</td>
<td></td>
</tr>
<tr>
<td>- Biomass &gt; Syngas &gt; Fischer Tropsch</td>
<td>study phase</td>
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Characteristics of steam cracking
What is steam cracking?

Steam cracking is a pyrolysis process.

A hydrocarbon mixture is heated in metal tubes inside a furnace in the presence of steam to a temperature at which the hydrocarbon molecules thermally decomposes.

For ethane the primary reaction is dehydrogenation $\text{C}_2\text{H}_6 \rightarrow \text{H}_2\text{C}=\text{CH}_2 + \text{H}_2$

Other free radical reactions also occur:
- Cracking and dehydrogenation of longer molecules resulting in hydrogen, methane, ethylene, propylene, butadiene and heavier.
- Continued dehydrogenation to form acetylene, aromatics and coke.

These reactions require a residence time of less than one second and are endothermic.
Principle of the cracking process

Saturated Hydrocarbons

\[
\begin{align*}
\text{H - C - C - C - ... - C - H} \\
\text{H - H - H - H}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2 - \text{C} - \text{C} - \text{C} - \text{H}_2 \\
\text{H}_2 - \text{C} - \text{C} - \text{H}_2
\end{align*}
\]

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

Cracking

Waste heat
SHP steam

Energy

Furnace
ca. 800°C
2-3 bar

Cracked gas
mainly unsaturated HC’s

- Hydrogen
- Paraffines
- Olefines
- Diolefines
- Aromatics
- Water

\[
\begin{align*}
\text{H}_2, \text{CH}_4, \text{CO}, \\
\text{C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \\
\text{C}_3\text{H}_4, \text{C}_3\text{H}_6, \text{C}_3\text{H}_8, \\
\text{C}_4, \text{C}_4'', \text{C}_4'', \\
\text{C}_5, \text{C}_5'', \text{C}_5''', \\
\text{C}_6, \text{C}_6'', \text{C}_6''', \\
\text{C}_n, \text{C}_n'', \text{C}_n'''
\end{align*}
\]
Key words for cracking

- **Yield**
- **Product/Feed**

- **Cracking severity**
  - Propylene/Ethylene ratio
    (used for liquid feed)
  - Conversion
    (used for gas feeds)

- **Depth of cracking**
  e.g. P/E=0,45  T~ 850 C; P/E=0,60  T~ 810 C

- **Conversion rate of feed component**
  e.g. 60-70 % for ethane

- **Dilution steam ratio**
  e.g. 0,5 kg/kg for naphtha

- **Steam/HC feed**

- **Residence time of one molecule in the cracking coil**
  e.g. 0,1 – 0,5 sec

- **Run time**
  Time between two decokings
  e.g. 50 – 80 days
Cracking conditions

- **Residence time** 0,1 – 0,5 sec
  - Short residence time favours primary reactions where olefins are formed
  - Long residence time favours secondary reactions where olefins are destroyed

- **Pressure** 2 – 3 bar
  - High pressure favours secondary reactions
  - Low pressure favours primary reactions

- **Dilution steam** 0,3 – 0,8 kg/kg
  - Reduces partial pressure of HC
  - Suppresses secondary reactions
  - Prevents excessive coke formation
  - Heavier feedstock needs more steam

- **Temperature** 800 – 850 C
  - High temperature promotes the formation of lower olefins, low temperatures favour oligomerization
  - Fast temperature rise favours ethylene and propylene
  - The heavier the feed the lower the temperature – coke formation!
Severity vs. product yield

Yields for naphtha feed

![Graph showing yields for naphtha feed with bars for different products like Ethylene, Propylene, Hydrogen, Fuel gas, C4, Gasoline, and Oil. The graph includes different P/E ratios (0.4, 0.5, 0.6) depicted in various colors.]
Raw materials and products
Wide range of feedstocks

- **Gaseous feeds**
  - Ethane
  - Propane
  - N-butane/i-butane

- **Liquid feeds**
  - Condensates from natural gas
  - Naphtha
  - Atmospheric gas oil (AGO)
  - Hydrocracker residue (HCR), hydrogenated vacuum gas oil (HVGO)
Liquid feeds

Main components

- Paraffins
- Naphthenes
- Olefins and aromatics (associated components in heavy feedstocks)
# Cracked gas composition vs. feedstock

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<tr>
<th></th>
<th>Ethane</th>
<th>Propane</th>
<th>n-c4/i-c4</th>
<th>Naphtha</th>
<th>AGO</th>
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<tr>
<td>H₂ + CO</td>
<td>4.06</td>
<td>1.70</td>
<td>1.23</td>
<td>1.03</td>
<td>0.71</td>
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<tr>
<td>CH₄</td>
<td>3.67</td>
<td>23.37</td>
<td>21.75</td>
<td>15.35</td>
<td>10.69</td>
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<tr>
<td>C₂H₂</td>
<td>0.50</td>
<td>0.67</td>
<td>0.50</td>
<td>0.69</td>
<td>0.34</td>
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<tr>
<td>C₂H₄</td>
<td>52.45</td>
<td>39.65</td>
<td>31.74</td>
<td>31.02</td>
<td>24.85</td>
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<tr>
<td>C₂H₆</td>
<td>34.76</td>
<td>4.57</td>
<td>3.67</td>
<td>3.42</td>
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<tr>
<td>C₃H₆ + C₃H₄</td>
<td>1.15</td>
<td>13.28</td>
<td>19.85</td>
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<tr>
<td>C₃H₈</td>
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<td>7.42</td>
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<td>0.38</td>
<td>0.31</td>
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<tr>
<td>C₄</td>
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<td>4.03</td>
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<td>9.54</td>
<td>9.61</td>
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<td>Pyrolysis Gasoline</td>
<td>0.87</td>
<td>4.27</td>
<td>6.41</td>
<td>19.33</td>
<td>20.6</td>
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<tr>
<td>Pyrolysis Fuel Oil</td>
<td>0.16</td>
<td>1.11</td>
<td>1.26</td>
<td>3.01</td>
<td>15.78</td>
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</table>

wt %
Ethylene yield vs paraffin content

![Graph showing the relationship between ethylene yield and paraffin content. The x-axis represents the n-paraffin content in vegetable-based gasoline, in %, while the y-axis represents the ethylene yield, also in %.]
Considerations for feedstocks

- Paraffins are the best raw materials
- Lower carbon number gives higher ethylene yield
- Cracking severity influences product yield
- Steam crackers are mostly integrated into refineries therefore
  - both gaseous and liquid feeds are used,
  - profitability is very complex issue and evaluated together with refinery operation
Main and byproducts

Feedstock → Pyrolysis section → Crack gas → Recovery section

Hydrogen → Fuel gas → Ethylene → Propylene → C4 → Gasoline → Oil
Steam cracking processes
Steam cracking at TVK
Process design considerations

Ethylene process is one of most complex systems in petrochemical industry. The following challenges have to be faced:

- Safety first
- High energy efficiency and minimum environmental emissions
- Low production costs and low investment costs
- High plant reliability
- Simple operation
- Good maintainability
- Minimum losses
Olefins production block diagram
Material and energy streams at TVK Olefin-2

- Natural gas
- Steam
- Electric power
- Naphtha
- Gasoil
- LPG (propane, butane)
- Methane (to fuel gas)
- Hydrogen → TIFO
- Ethylene → PE production
- Propylene → PP production
- BT fraction → MOL
- C8 fraction → MOL
- C9+ fraction → MOL
- Quench oil → CTK
- Ethane (repyrolysis)
- Propane (repyrolysis)
- C4/C5 (repyrolysis)
Tasks of a cracking furnace

- Production of ethylene and propylene by endothermic cracking reaction
- Preheating of feed and dilution steam by utilization of waste heat
- Cooling of the cracked gas to freeze chemical reactions
- Production of superheated HP steam by utilization of waste heat
Cracking furnaces

- Radiant section: thermal cracking reactions (800 – 850 °C)
- Convection section: heat recovery from hot flue gas
  - Feed preheating
  - Boiler feed water preheating
  - Process steam superheating
  - HHP steam superheating
- Linear quench exchanger
  - Freezing cracking reactions in order to avoid product losses by secondary reactions (400 - 600 °C)
  - Heat recovery -> HHP steam production
- Olefin-1 and Olefin-2 represent two generations
  - O-1: 11 furnaces
  - O-2: 4 furnaces
Cracking furnace in Olefin-2

- Quench exchangers
- Convection section
- Radiant coils
- Side-wall burners
- Floor burners
Tube arrangement in the radiant zone (Olefin-2)

- Inlet tubes
- Outlet tubes
- Y-fitting
- S-shaped bends
- Floor burners
Oil and water quench

Further **cracked gas cooling** by direct oil injection downstream the quench coolers (220 - 250 °C)

**Oil Fractionation (primary fractionation) and Quench Oil Cycles**

- Two quench oil cycles (Pyrolysis Fuel Oil and Pyrolysis Gas Oil) are used as heat carrier to cool the cracked gas (~100 °C) and to shift the recovered heat to consumers
- Both quench oil cycles are formed by condensing the heavy ends of the cracked gas
- Process steam generation by hot quench oil

**Water Scrubbing (Water quench column)**

- Cracked gas is cooled by water circulation to ambient (~30 °C) temperature to condense heavy gasoline and process (dilution) steam
- Circulating water is withdrawn from the bottom of the column and pumped to several consumers for low temperature heat recovery
Hot section: Oil fractionating and water quench column in O-2
Cracked gas compression

- **Cracked gas is compressed** with a 5-stage centrifugal compressor
  - Suction pressure: 0.5 bar (g)
  - Discharge pressure: 32-36 bar (g)

- **The compressor** is driven by an extraction/condensation steam turbine.

- Process water and gasoline are condensed in the interstage **coolers** and knocked out in the interstage **separators**. Gasoline is directed to hydrogenation and separation.

- **Caustic Scrubbing**: removal of the acid components CO2 and H2S in a 3-stage caustic scrubber
Cracked gas compressor in Olefin-2
Cold section block diagram
Cold section 1

- **Precooling, drying, deethanizer**
  - Cracked gas cooling to drying temperature
  - Cracked gas *drying* to eliminate water content
  - Cooling to -40 °C (cooling with propylene refrigerant and cold streams from the low temperature section)
  - Separation of C2- and C3+ fraction (deethanizer)

- **C3+ processing**
  - C3/C4+ separation (depropanizer)
  - C3 hydrogenation: conversion of methyl-acetylene and propadiene to propylene and propane
  - C3H6/C3H8 separation: *propylene* product, propane recycle
  - C4/C5 separation
Cold section 2

- **C2 hydrogenation**
  - Acetylene is selectively hydrogenated to ethylene
  - Max. 1 ppm acetylene downstream the catalytic reactor

- **Low temperature section (cold train)**
  - C2- fraction is cooled with ethylene refrigerant and expanded cold streams (-145 C)
  - Separation of C2 from C1 and hydrogen from methane: ethylene, ethane, and almost all methane is condensed, the remaining gas consists of a hydrogen-rich fraction

- **C2 splitter**
  - To separate ethylene (top product) and ethane (recycled to feed)
Safety aspects
About safety

- Safety first concept has to be applied for a plant during
  - design,
  - construction and
  - operation
in line with the industrial standards and norms

- Safety is expensive – there is nothing for free
Major risk factors in olefin plants

- High volume of highly flammable hydrocarbon gases and liquids
- Extremely high and low temperatures
- High pressure
- Corrosion
- Complexity of operation
Plant safety: based on risk evaluation

Risk consideration

- Frequency of hazardous events
- Consequence of hazardous events

Process risk

Risk matrix

- Frequency
  - Low
  - Medium
  - High
- Consequence
  - Low
  - Medium
  - High
Risk reduction

Levels of risk reduction measures

- **Incident**
  - remote with very serious consequences
  - failure of safety system

- **Failure**
  - seldom with serious consequences
  - failure of control system, failure of plant components, severe operating failures

- **Process upset**
  - frequent with minor consequences
  - failure of control system, utility system, simple operating failure

- **Process variation**

- **Emergency Response**
  - Emergency Response Plan
  - Fire Brigade/First Aid

- **Mitigation**
  - Mechanical System
    - (e.g. safety valves, blow-down system)
  - Safety Instrumented System

- **Prevention**
  - Inherent Design
  - Mechanical System
  - Safety Instrumented System
  - Operating Instruction

- **Control and Monitoring**
  - Basic Process Control System
  - Monitoring System (process alarms)

- **Process**
  - Operating condition
  - Normal Operation
  - Start-up/Shut-down
Example for risk reduction: selection of construction materials

Suitable material is not subject to unexpected material related failures during the calculated plant lifetime under nominal operation conditions

- Calculated plant lifetime: ~15-20 Years
- Nominal operation conditions:
  - Specified cases of operation
  - Design pressure and temperatures, fluid composition, flow velocity as specified
  - Start up
  - Shut down
  - Site condition
Example for risk reduction: fire and explosion protection

- Proper selection of mechanical equipment to avoid leakages
- Explosion proof electric equipment and instrumentation
- Gas detection systems
- Steam curtains (e.g. for the furnaces)
- Closed blow-down system
- Safety distances between plant section
- Fire proofing insulation
- Fire water systems including hydrants and monitors
- Water spray systems
Control systems
The automation pyramid of a company
Plant control systems
Key equipment
Main groups of equipment

- Furnaces
- Static equipment
  - Columns, reactors and other pressure vessels
  - Heat exchangers
  - Storage tanks
- Rotating equipment
  - Turbo machineries
    - Turbo compressors
    - Steam turbines
  - Reciprocating compressors
  - Pumps
Turbo compressors in O-2 plant

- **Crack gas compressor**
  - Duty: 13,5 MW
  - Drive: steam turbine

- **Ethylene compressor**
  - Duty: 6,5 MW
  - Drive: steam turbine

- **Propylene compressor**
  - Duty: 4,5 MW
  - Drive: steam turbine
Crack gas compressor O-2 plant

1st stage
0,3 → 1,5 bar

2nd and 3rd stage
1,35 → 9,3 bar

4th and 5th stage
9,0 → 36 bar
Crack gas compressor O-2 plant
Crack gas compressor LP section
Steam turbine
Turbine driven BFW pump
Multistage BFW pump
Overview of investment and operating costs
Investment costs
Basis: WE 2010 Q1      Capacity: 800 kt

<table>
<thead>
<tr>
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<tr>
<td>ISBL</td>
<td>704</td>
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<tr>
<td>OSBL</td>
<td>352</td>
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<tr>
<td>Other project cost</td>
<td>400</td>
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<tr>
<td>Total investment</td>
<td>1 456</td>
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<td>EUR/t Ethylene</td>
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<td>Specific cost</td>
<td>1820</td>
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Ethylene production cost  
Basis: WE 2010 Q1/Q2  Capacity: 800 kt

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<thead>
<tr>
<th>Raw material less coproduct</th>
<th>Total utility costs</th>
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<td>Total direct fix costs</td>
<td>Total allocated fix costs</td>
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### PRODUCTION COST SUMMARY

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<tr>
<th>Quantity</th>
<th>Units</th>
<th>2010 Q1</th>
<th>2010 Q2</th>
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<td>Naphtha</td>
<td>3,230 ton</td>
<td>1 651,1</td>
<td>1 755,0</td>
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<td>Catalyst &amp; Chemicals</td>
<td>3,6</td>
<td>4,0</td>
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<td><strong>Total Raw Materials Costs</strong></td>
<td></td>
<td>1 655</td>
<td>1 759,0</td>
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<td>Fuel</td>
<td>0,587 ton</td>
<td>195,1</td>
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<td>High Pressure Steam (40 bar)</td>
<td>0,750 ton</td>
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<td>Cooling Water</td>
<td>0,454 kton</td>
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<td>Electricity</td>
<td>0,084 MWh</td>
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<td><strong>Total Utility Costs</strong></td>
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<td>Propylene</td>
<td>(0,516) ton</td>
<td>( 427,5)</td>
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<tr>
<td>Fuel (FOE)</td>
<td>(0,813) ton</td>
<td>( 270,2)</td>
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<td>Benzene</td>
<td>(0,239) ton</td>
<td>( 172,9)</td>
<td>(201,0)</td>
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<td>C7 - C9 cut</td>
<td>(0,267) ton</td>
<td>( 139,6)</td>
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<td>Butadiene</td>
<td>(0,148) ton</td>
<td>( 137,4)</td>
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<td>Other</td>
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<td><strong>Total Co-Products</strong></td>
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