OLEFIN PRODUCTION

Olefins by steam cracking
Content

- 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
- Global production in 2015 is about 143 million tons ethylene and 95 million tons propylene
- 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

- Ethylene: 60%
- Ethylene oxide: 14%
- EDC (PVC): 12%
- Styrene: 6%
- VAM: 1%
- Others: 7%
Building block for petrochemicals – propylene consumption

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

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

OLEFIN-1
370 kt/yr

OLEFIN-2
290 kt/yr

BUTADIENE
130 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

PROPYLENE TO SPC

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

FUEL OIL TO CARBON BLACK PRODUCER

BUTADIENE TO CUSTOMERS

CUSTOMERS
History
Ethylene milestones

- 1913: Standard Oil’s scientist patented thermal cracking process
- 1930s: 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
- 1950s: 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
Olefins production by processes, 2008

- Ethylene production mainly through steam cracking
- Propylene production includes refinery operation and other processes

Legend:
- Red: Steam cracking
- Blue: Refinery operation
- Green: Others
Ethylene at MPK (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>
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<th>Process</th>
<th>Status</th>
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<tr>
<td>Steam cracking</td>
<td>dominating technology</td>
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<tr>
<td>Refinery processes</td>
<td>minor importance for ethylene important for propylene only</td>
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<tr>
<td>MTO Methanol to Ethylene and Propylene</td>
<td>technology is ready but not yet commercialized</td>
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<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 and Dehydration of Ethanol</td>
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<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

H H H
| | | | | |
H-C-C-C ... -C-H
| | | | |
H H H
| |

Cracking

Waste heat
SHP steam

Furnace
c.a.800°C
2-3 bar

Cracked gas
mainly unsaturated HC’s

Hydrogen
Paraffines
Olefinens
Diolefinens
Aromatics
Water

H₂, CH₄, CO,
C₂H₂, C₂H₄, C₂H₆,
C₃H₄, C₃H₆, C₃H₈,
C₄, C₄”, C₄””,
C₅, C₅”, C₅””,
C₆, C₆”, C₆””,
Cₙ, Cₙ”, Cₙ””,
Key words for cracking

- **Yield**
- **Cracking severity**
  - Propylene/Ethylene ratio
    (used for liquid feed)
  - Conversion
    (used for gas feeds)
- **Dilution steam ratio**
- **Residence time**
- **Run time**

**Product/Feed**

- **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
- **Steam/HC feed**
  - e.g. 0.5 kg/kg for naphtha
- **Residence time of one molecule in the cracking coil**
  - e.g. 0.1 – 0.5 sec
- **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

- Ethylene
- Propylene
- Hydrogen
- Fuel gas
- C4
- Gasoline
- Oil
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)
Yields depend on feed

![Graph showing yields depending on feed](image)

- **Ethane**
- **Propane**
- **Butanes**
- **Naphtha**
- **AGO**

Olefins in cracked gas, %

Average C number of feed

- Ethylene
- Propylene
Ethylene yield vs paraffin content
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

- Pyrolysis section
  - Feedstock
  - Steam
  - Crack gas

- Recovery section
  - Hydrogen
  - Fuel gas
  - Ethylene
  - Propylene
  - C4
  - Gasoline
  - Oil
Steam cracking processes
Steam cracking at MPK
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 MPK 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
Tube arrangement in the radiant zone (Olefin-2)
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
Cold section block diagram

Feedstock → Cracking and Quenching → Oil and Water Quench → Cracked Gas Compression → Precooling Drying Deethanizer → C2 Hydrogenation → Cold Train Demethanizer → C2H4/C2H6 Separation

- Ethane Recycle
- C2-
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
- Risk matrix

Risk matrix:

- Consequence
- Frequency
- Process risk

Frequency of hazardous events:
- low
- medium
- high

Consequence of hazardous events:
- 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**

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**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

- **Management level**
- **Operator level**
- **Controller level**
- **Field level**

**ERP**

**P&S**

**Supervision, Control, Data Acquisition,**

**Process control, PLC, PID, APC, Safety instrumentation,** etc.

**Sensors, Actuators, Switchgears,** etc.
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

kb₉ 13.4 MW
Crack gas compressor LP section
Steam turbine
Turbine driven BFW pump
Multistage BFW pump
Overview of investment and operating costs
Investment costs

Basis: WE 2015 Q2    Capacity: 825 kt
Standard naphtha cracker

- Investment costs    million EUR
  - ISBL                862
  - OSBL                431
  - Total investment:   1293

Specific investment 1567 EUR/ton
Ethylene production cost
Basis: WE 2015Q2  Capacity: 825 kt

<table>
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<tr>
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<th>EUR/ton</th>
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<tbody>
<tr>
<td>Raw materials</td>
<td>1116,7</td>
</tr>
<tr>
<td>Utilities</td>
<td>129,3</td>
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<tr>
<td>Co-products credit</td>
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<tr>
<td>Total variable cost</td>
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<td>Fix costs</td>
<td>82,6</td>
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<td>Total cash cost</td>
<td>384,1</td>
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