OLEFINS PRODUCTION

Olefins by steam cracking

Content

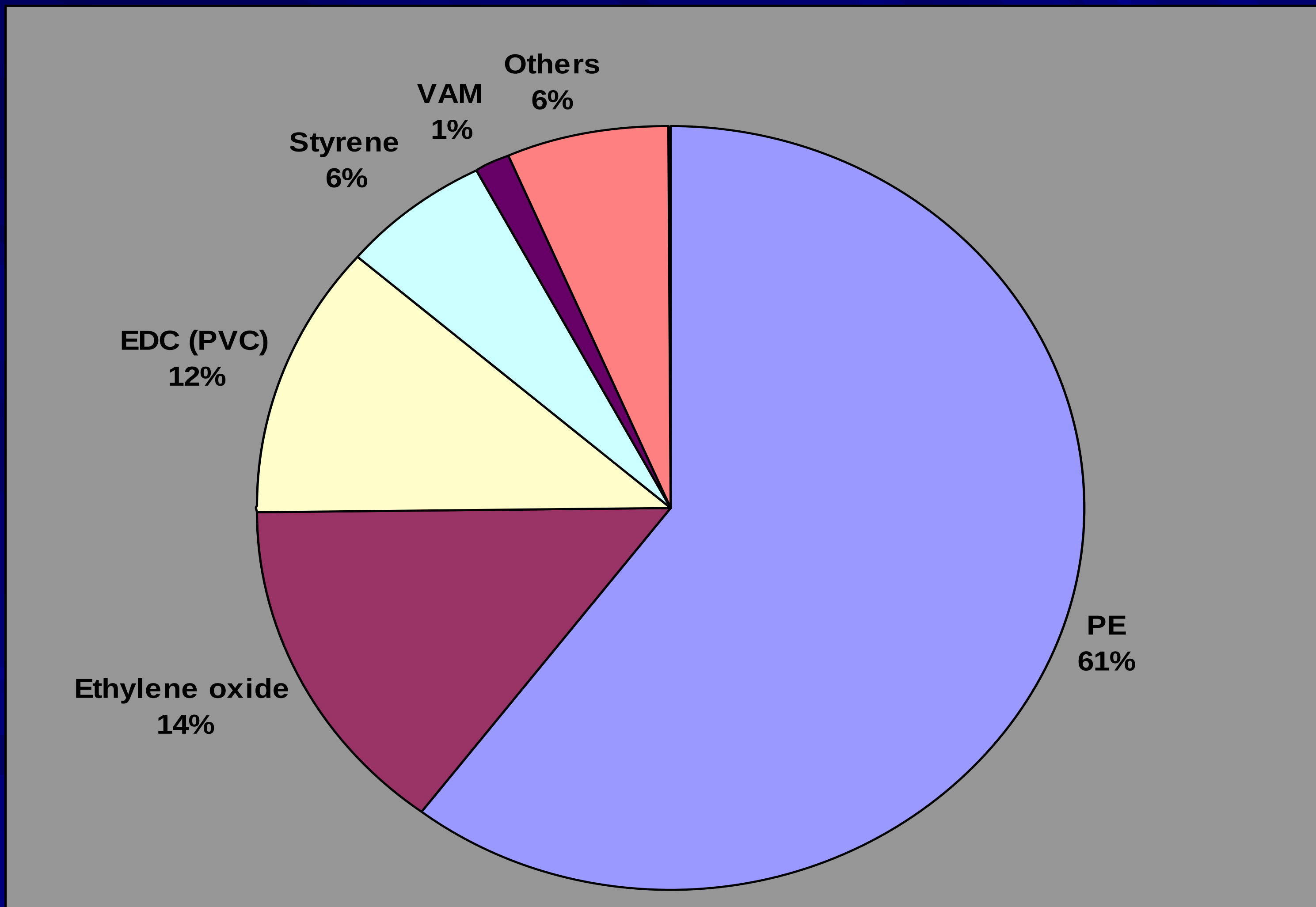
- Importance of ethylene and propylene in the chemical industry
- History
- Characteristics of steam cracking
- Raw materials and products
- Steam cracking processes, steam cracking at TVK
- Safety aspects
- Control systems
- Key equipment
- Overview of investment and operating costs

Importance of ethylene and propylene in the chemical industry

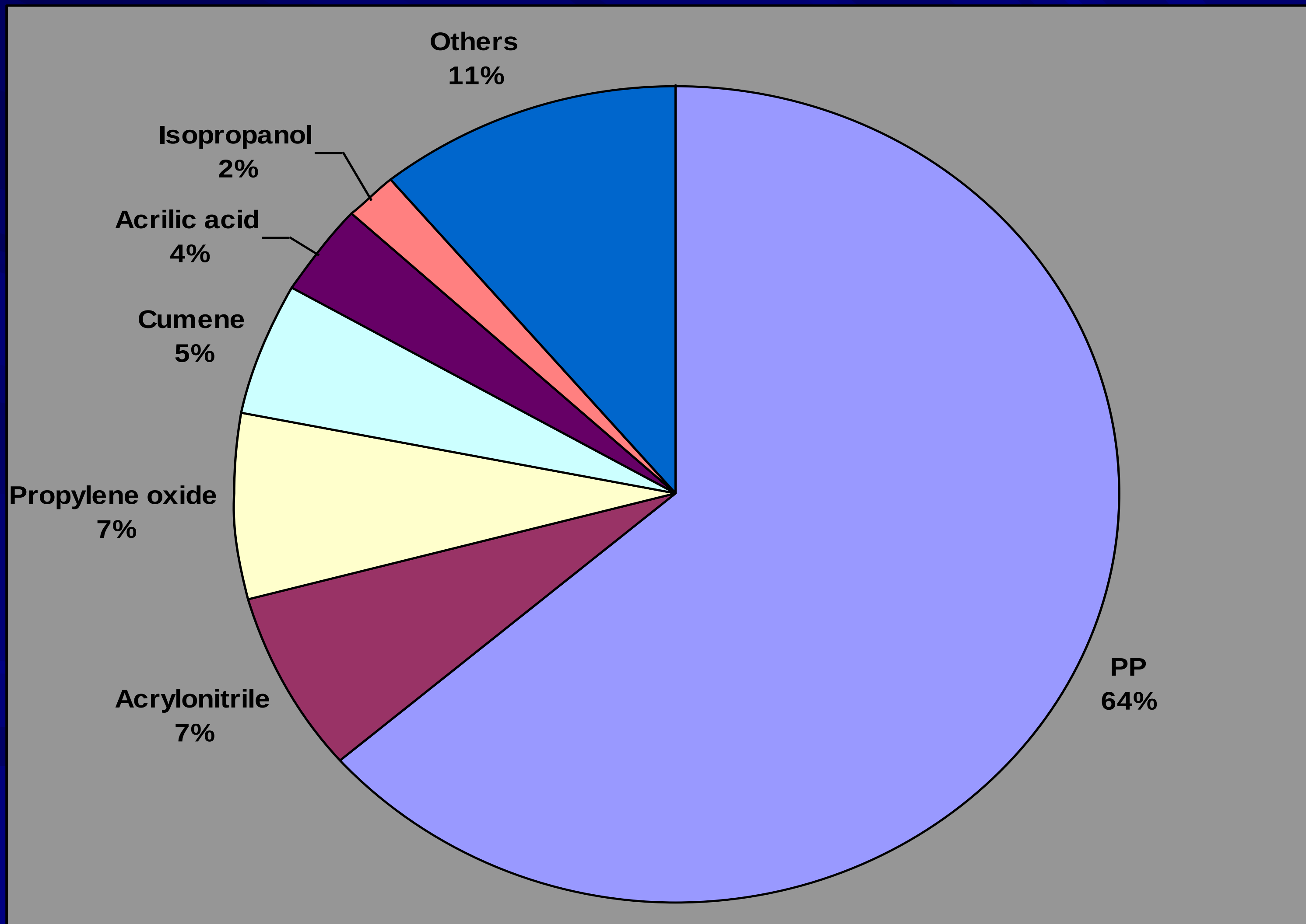
Lower olefins: ethylene and propylene

- The largest volume petrochemicals produced
- 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

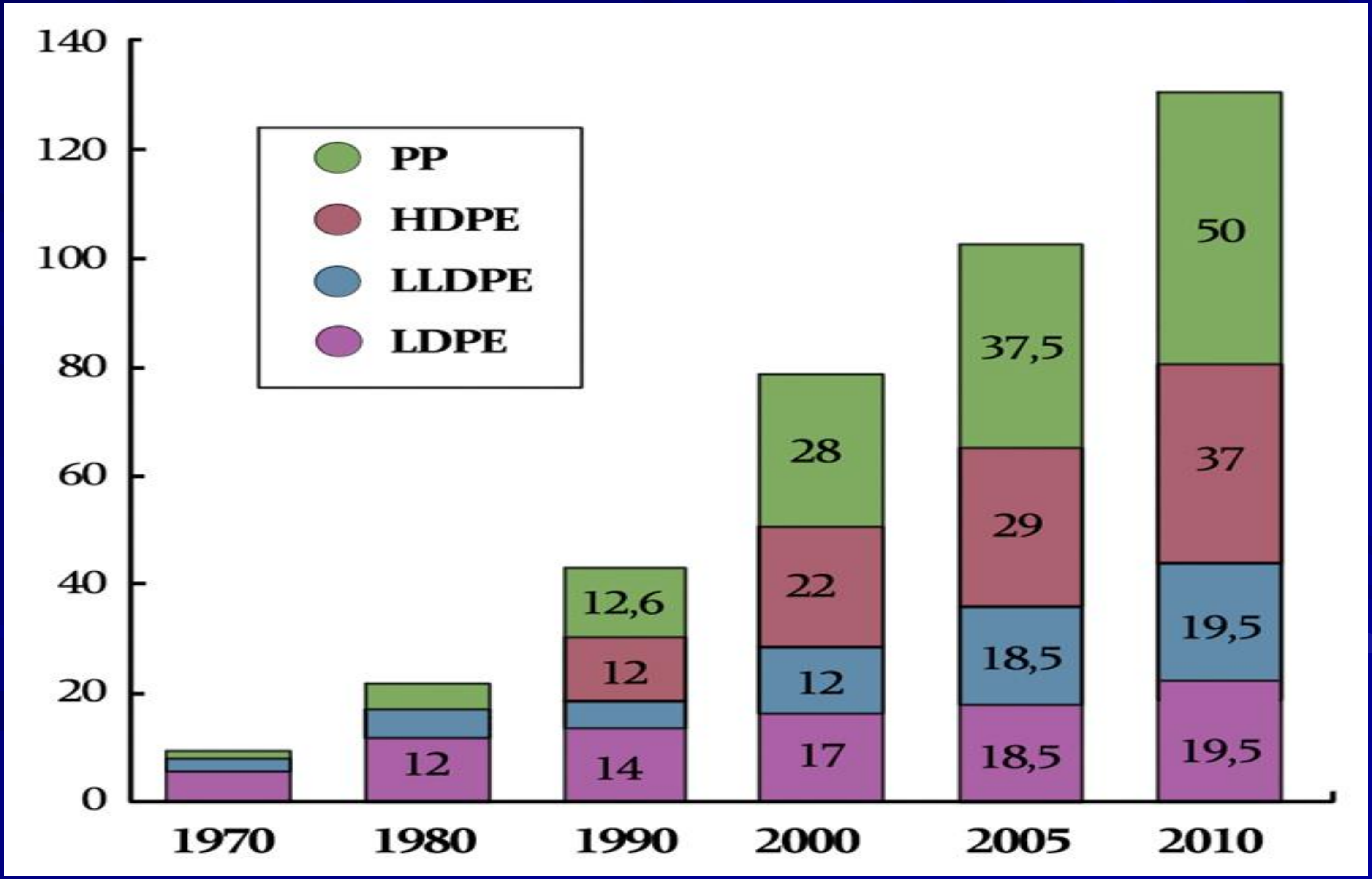
Building block for petrochemicals – ethylene consumption 2009



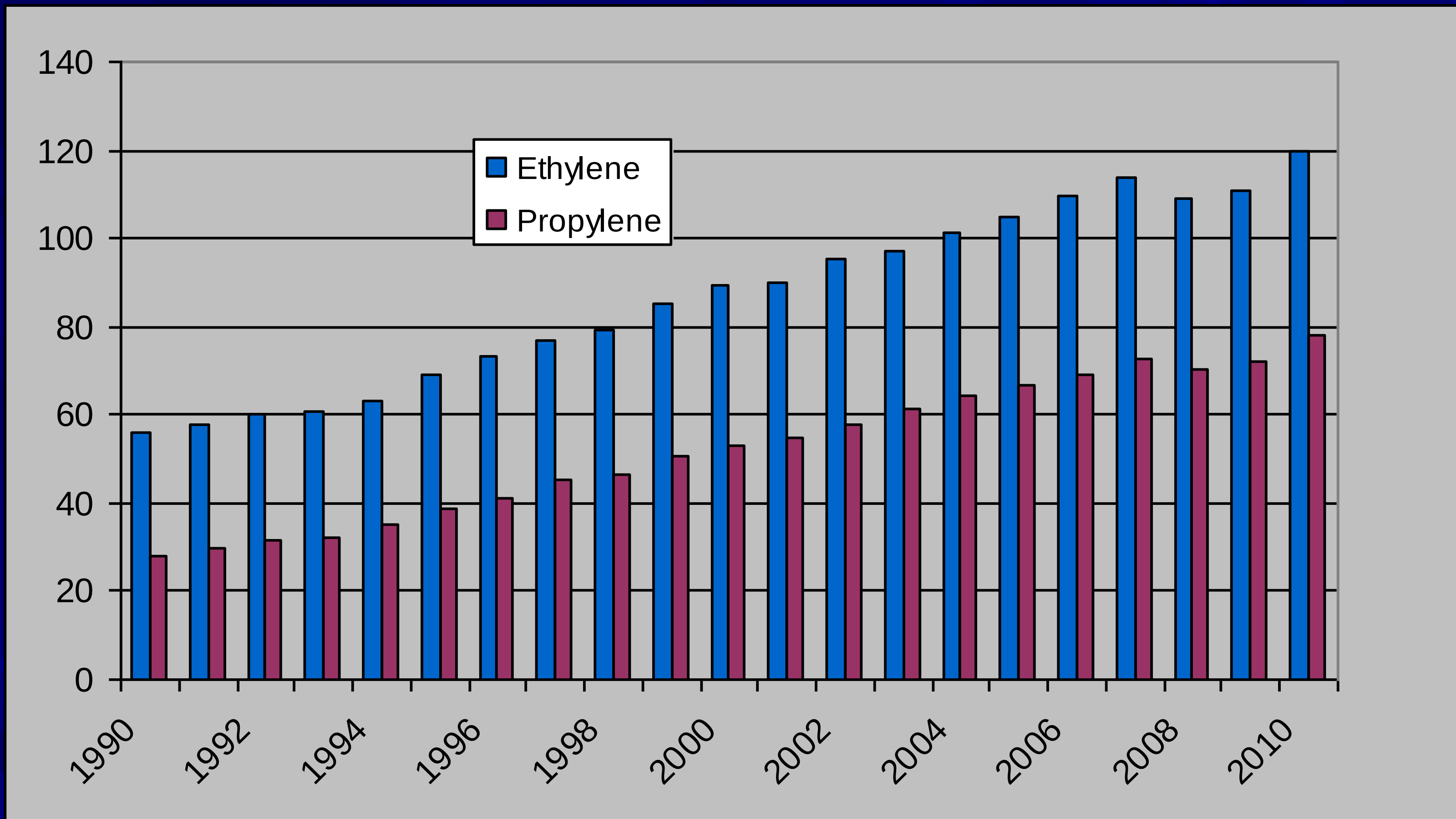
Building block for petrochemicals – propylene consumption 2009



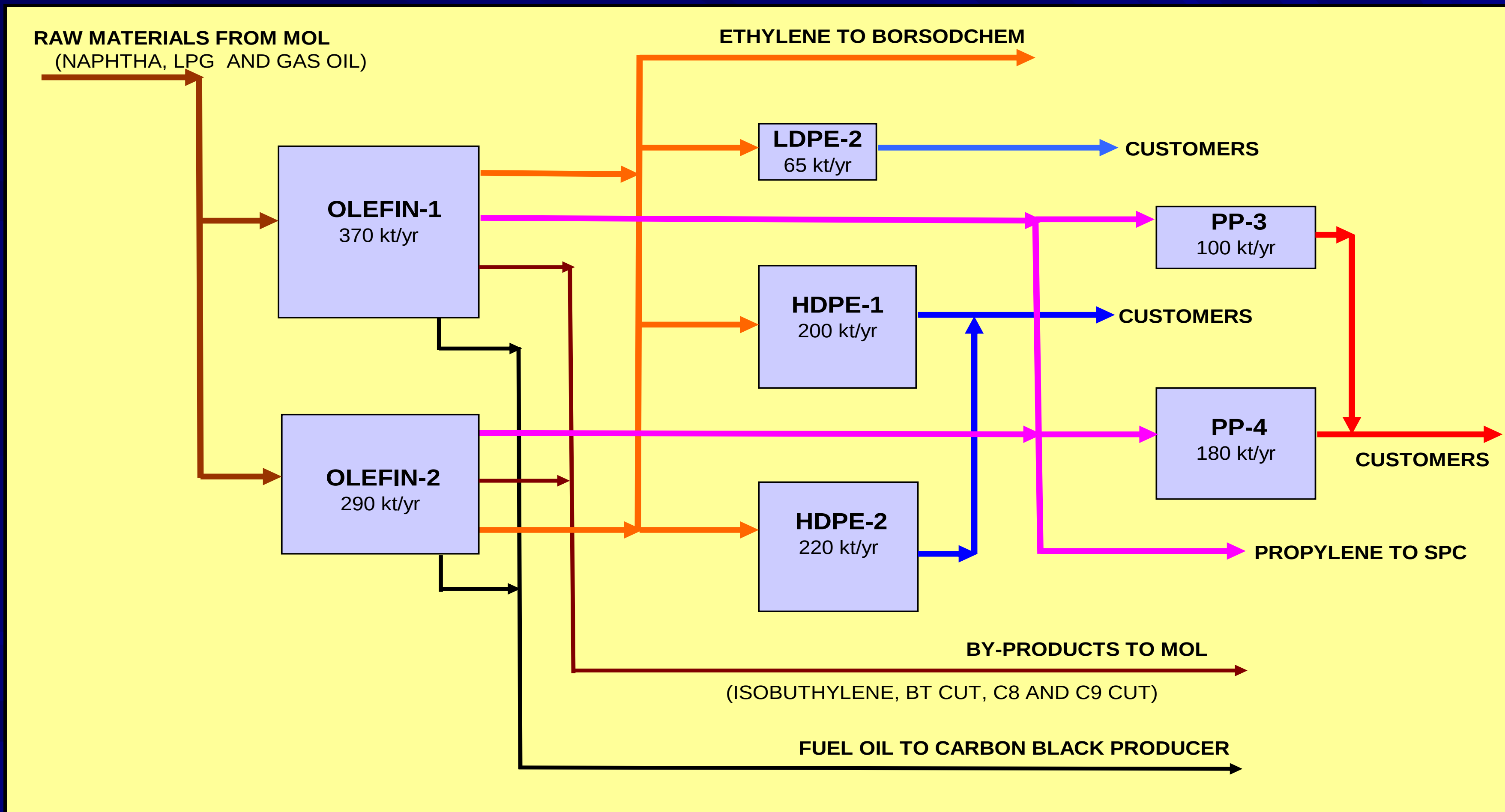
Main drivers for ethylene and propylene demand: PE and PP



Global consumption of ethylene and propylene



Hungary: ethylene produced by TVK only

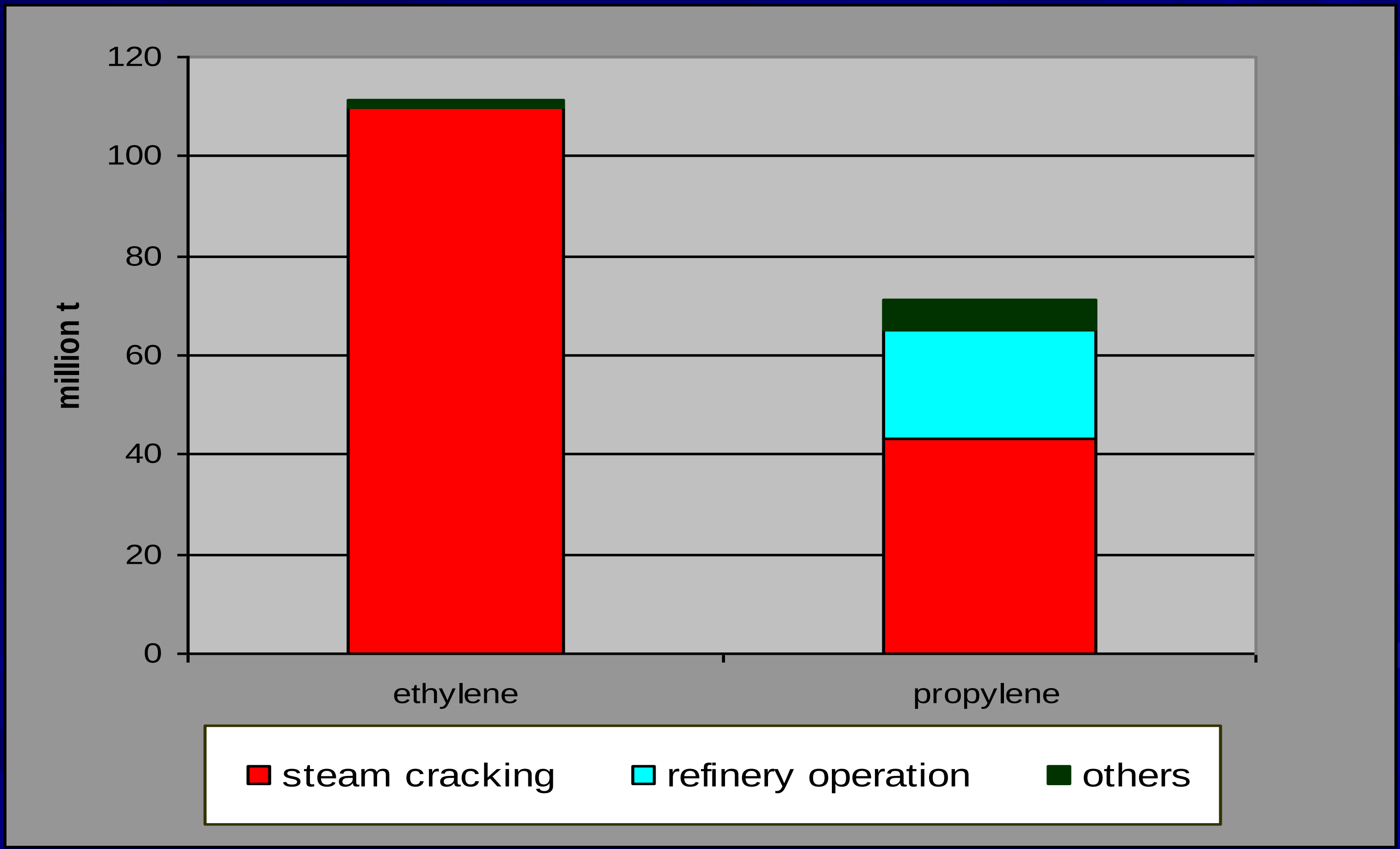


History

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 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

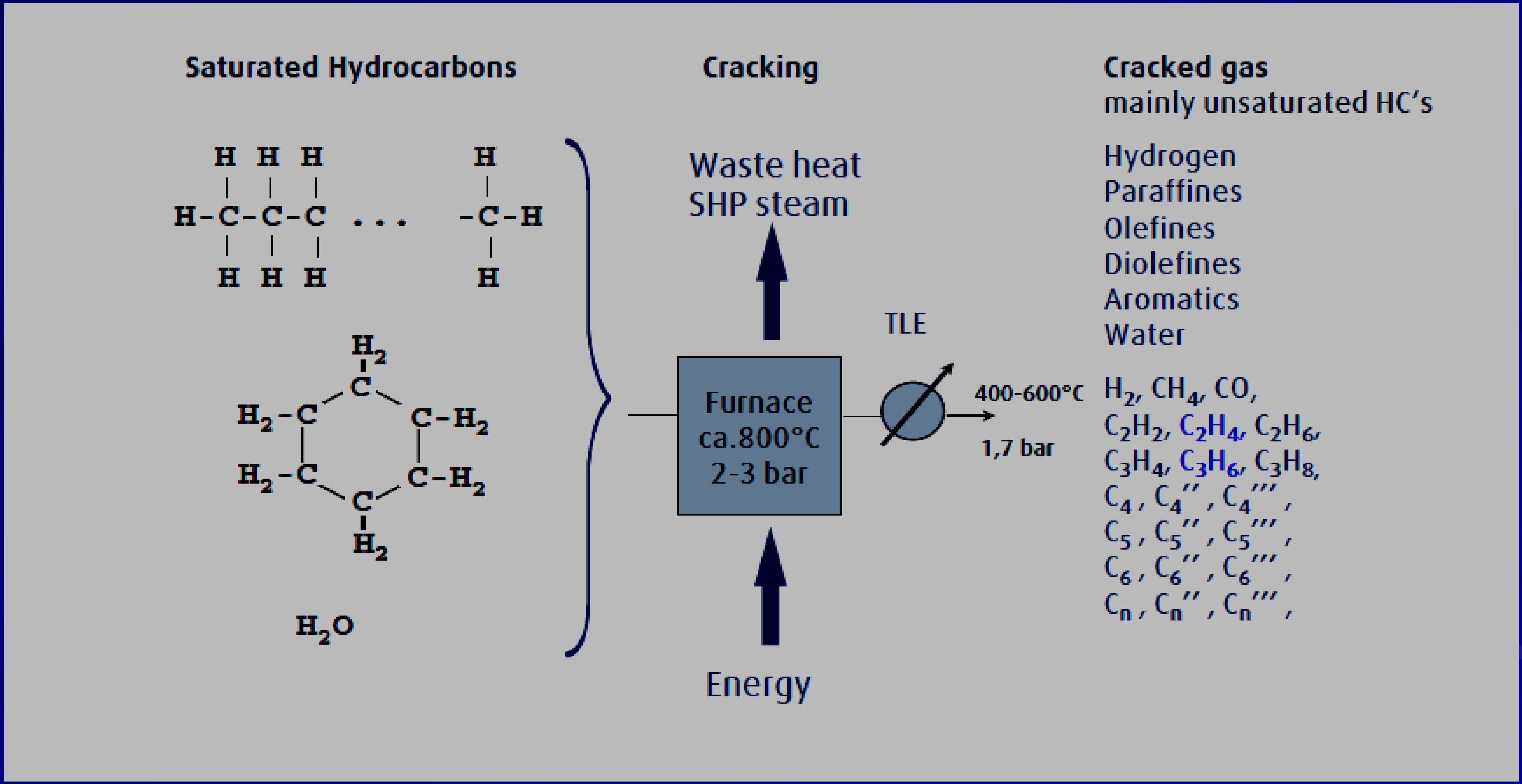
Steam cracking	dominating technology
Refinery processes	minor importance for ethylene important for propylene only
MTO Methanol to Ethylene and Propylene	technology is ready but not yet commercialized
MTP Methanol selectively to Propylene	commercialisation phase
Syngas via Fisher Tropsch	minor importance
Green Ethylene - Biomass via Fermentation to Ethanol and Dehydration of Ethanol - Biomass > Syngas > Fischer Tropsch	commercialisation phase study phase

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 $C2H6 \rightarrow H2C=CH2 + H2$
- 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



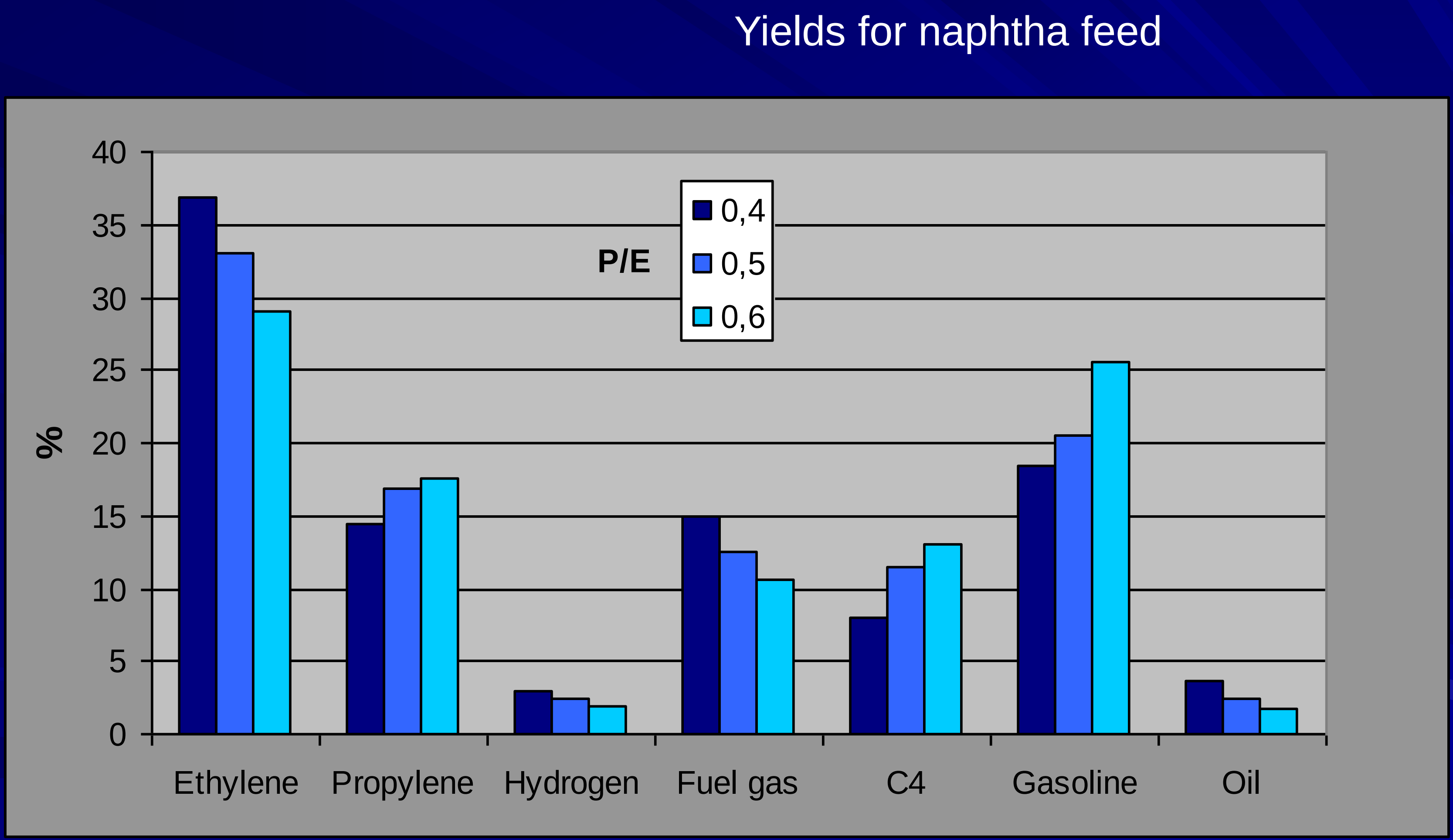
Key words for cracking

■ Yield	Product/Feed
■ Cracking severity	Depth of cracking
– Propylene/Ethylene ratio (used for liquid feed)	e.g. P/E=0,45 T~ 850 C; P/E=0,60 T~ 810 C
– Conversion (used for gas feeds)	Conversion rate of feed component e.g. 60-70 % for ethane
■ Dilution steam ratio	Steam/HC feed e.g. 0,5 kg/kg for naphtha
■ Residence time	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



Raw materials and products

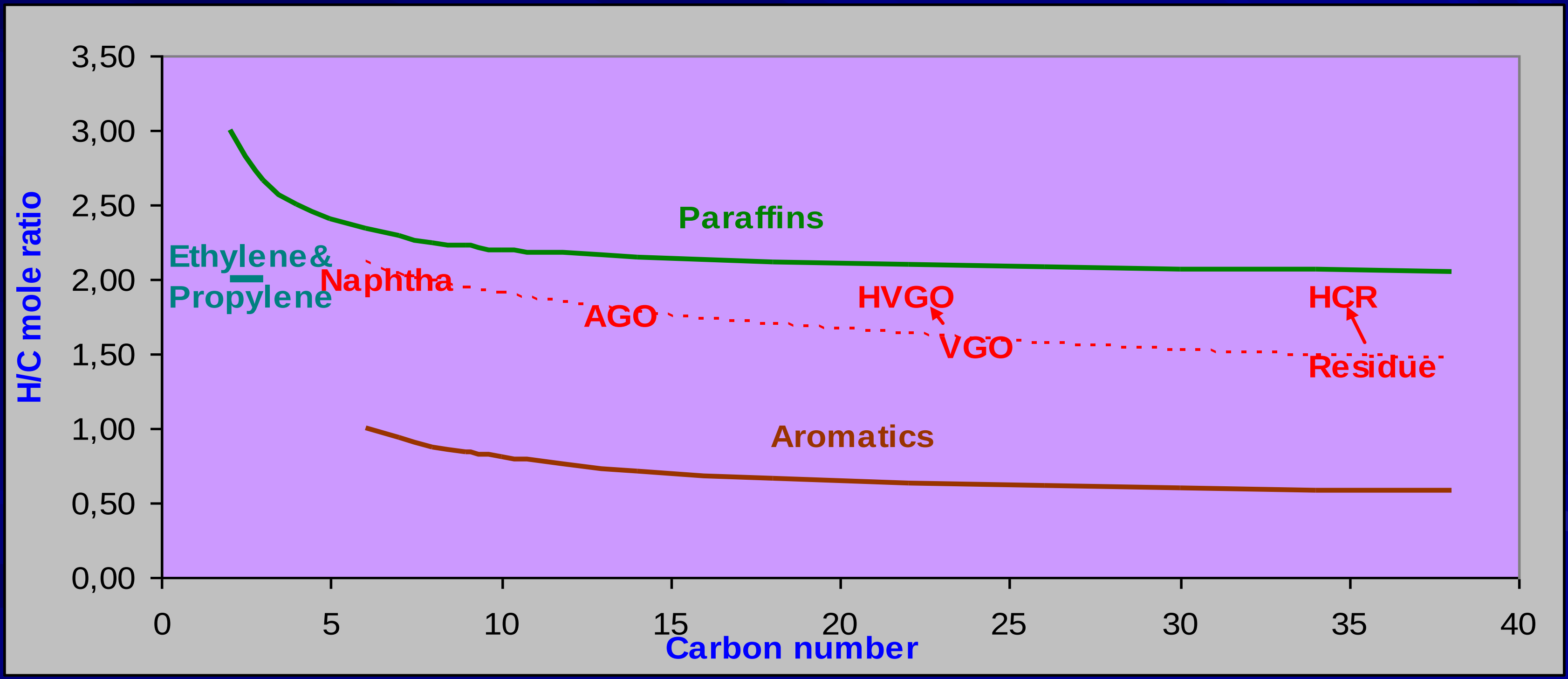
Wide range of feedstocks

- 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)

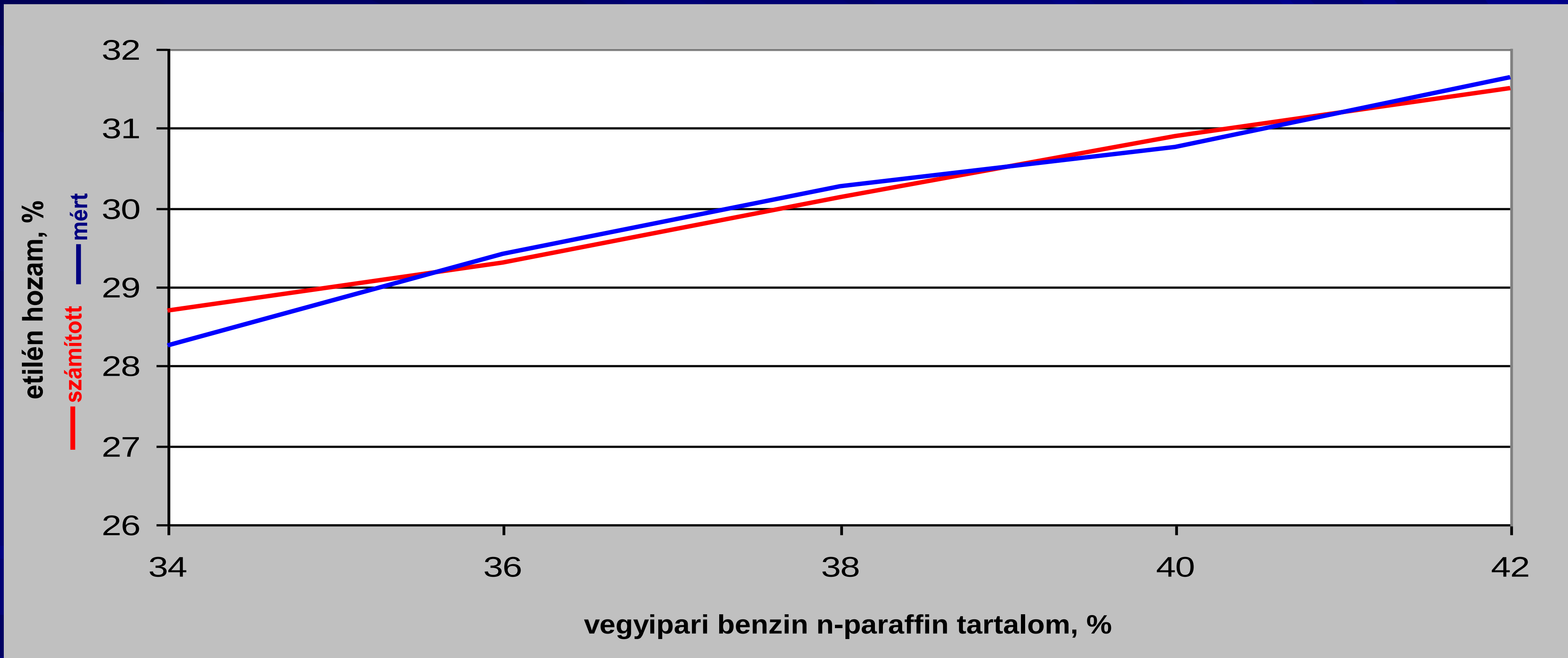


Cracked gas composition vs. feedstock

wt %

	Ethane	Propane	n-c4/i-c4	Naphtha	AGO
H2 + CO	4.06	1.70	1.23	1.03	0.71
CH4	3.67	23.37	21.75	15.35	10.69
C2H2	0.50	0.67	0.50	0.69	0.34
C2H4	52,45	39.65	31.74	31.02	24.85
C2H6	34.76	4.57	3.67	3.42	2.75
C3H6 + C3H4	1.15	13.28	19.85	16.21	14.28
C3H8	0.12	7.42	0.69	0.38	0.31
C4	2.24	4.03	12.90	9.54	9.61
Pyrolysis Gasoline	0.87	4.27	6.41	19.33	20.6
Pyrolysis Fuel Oil	0.16	1.11	1.26	3.01	15.78

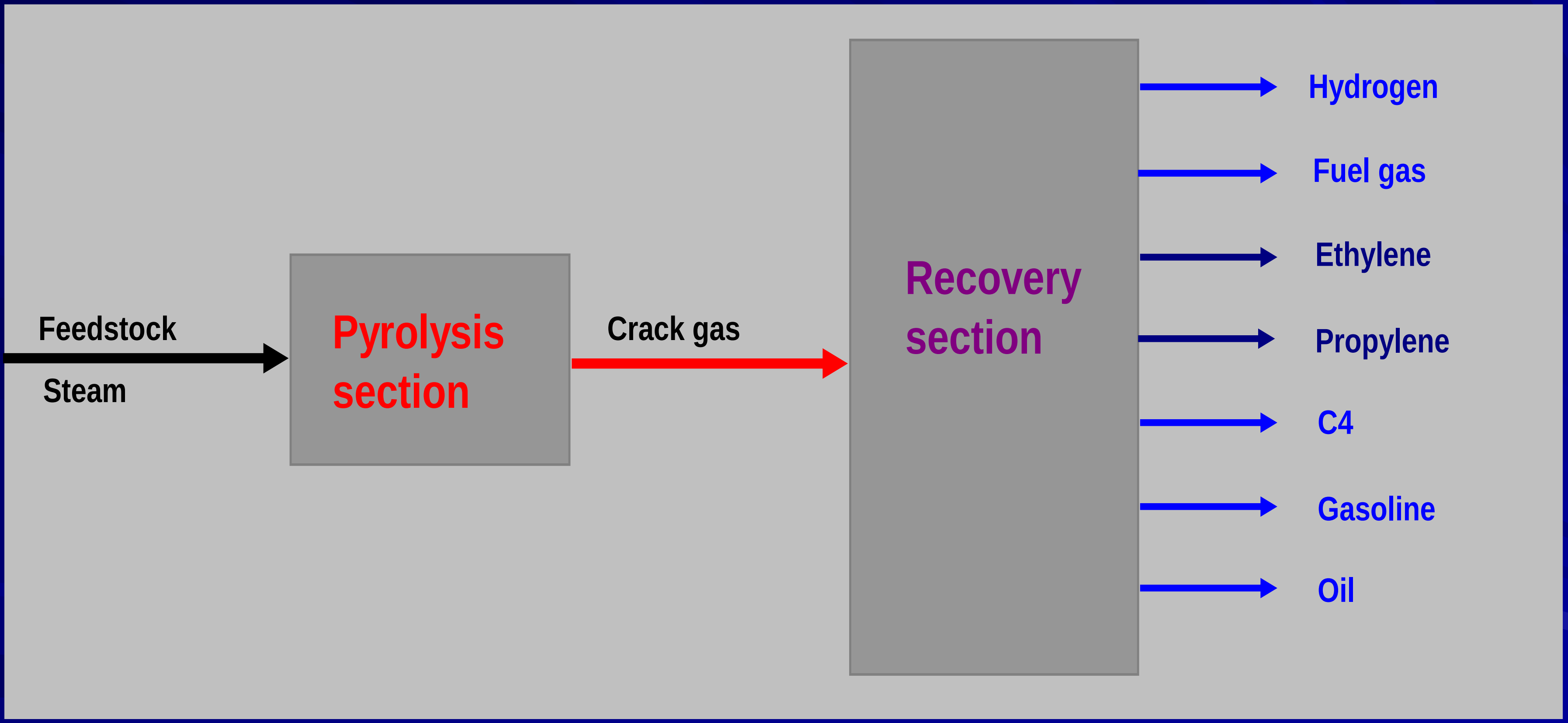
Ethylene yield vs paraffin content



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



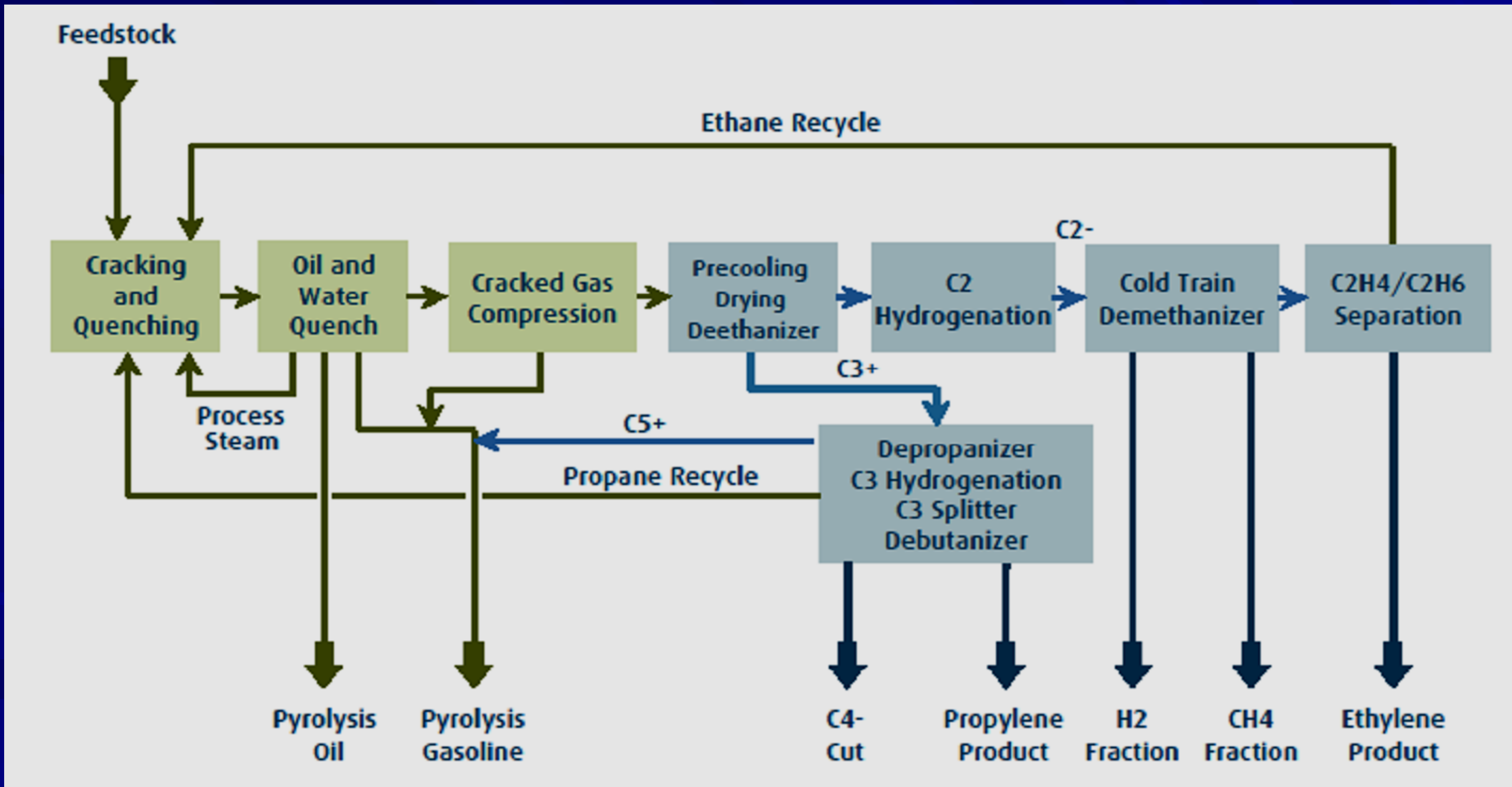
Steam cracking processes
Steam cracking at TVK

Process design considerations

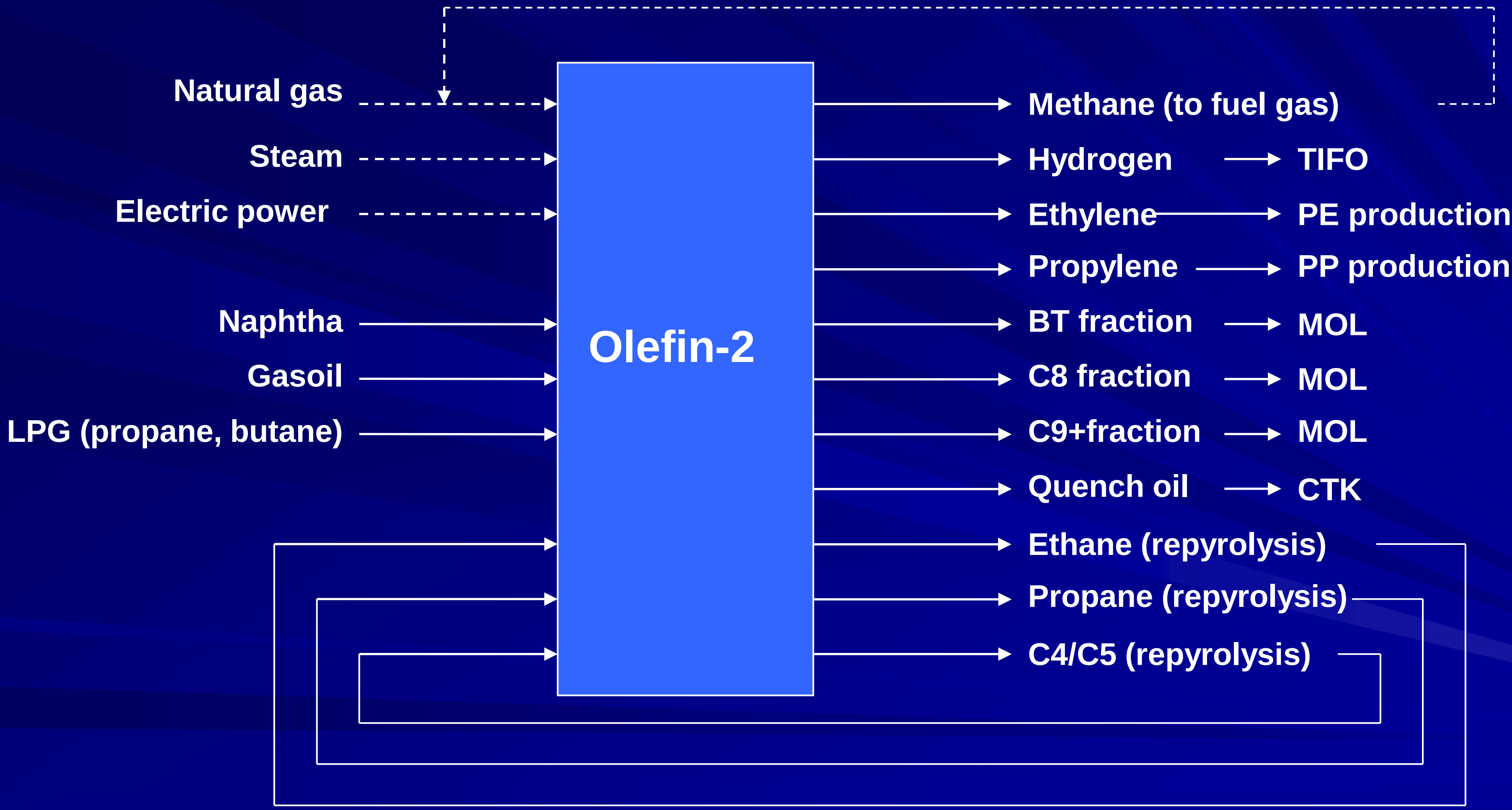
Ethylene process is one of most complex systems in petrochemical industry. The following challenges have to be faced:

- 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



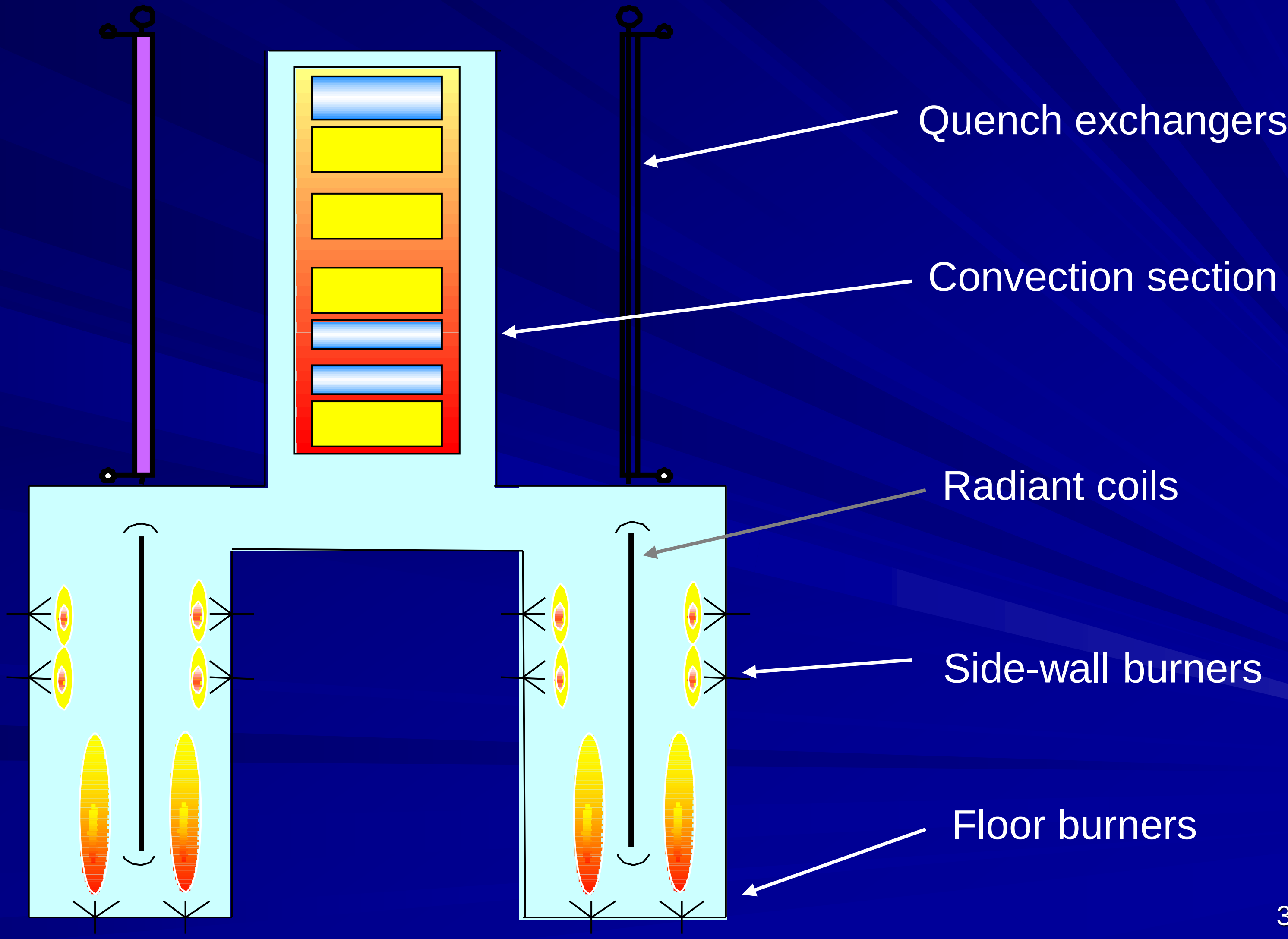
Tasks of a cracking furnace

- 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

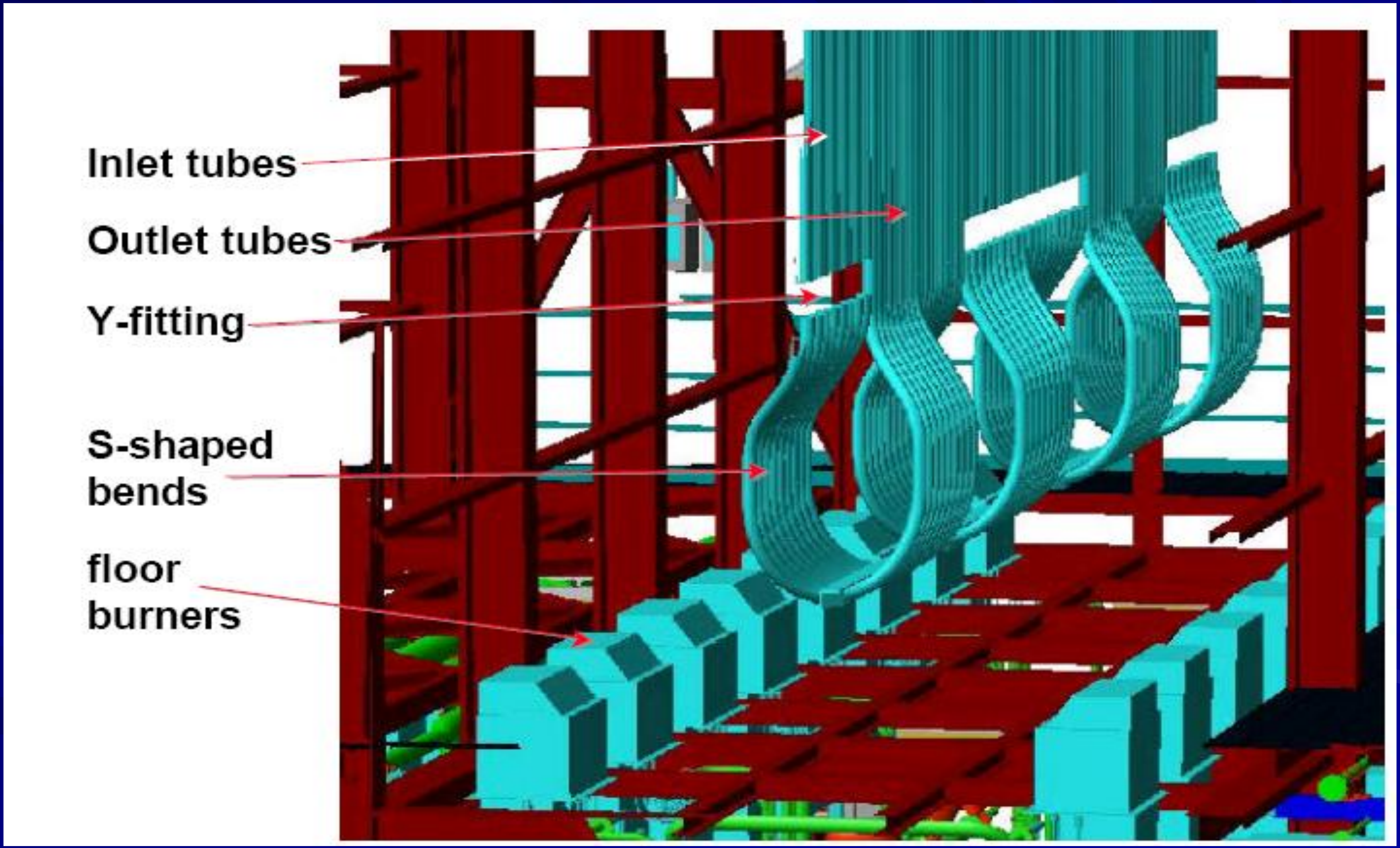
Cracking furnaces

- 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



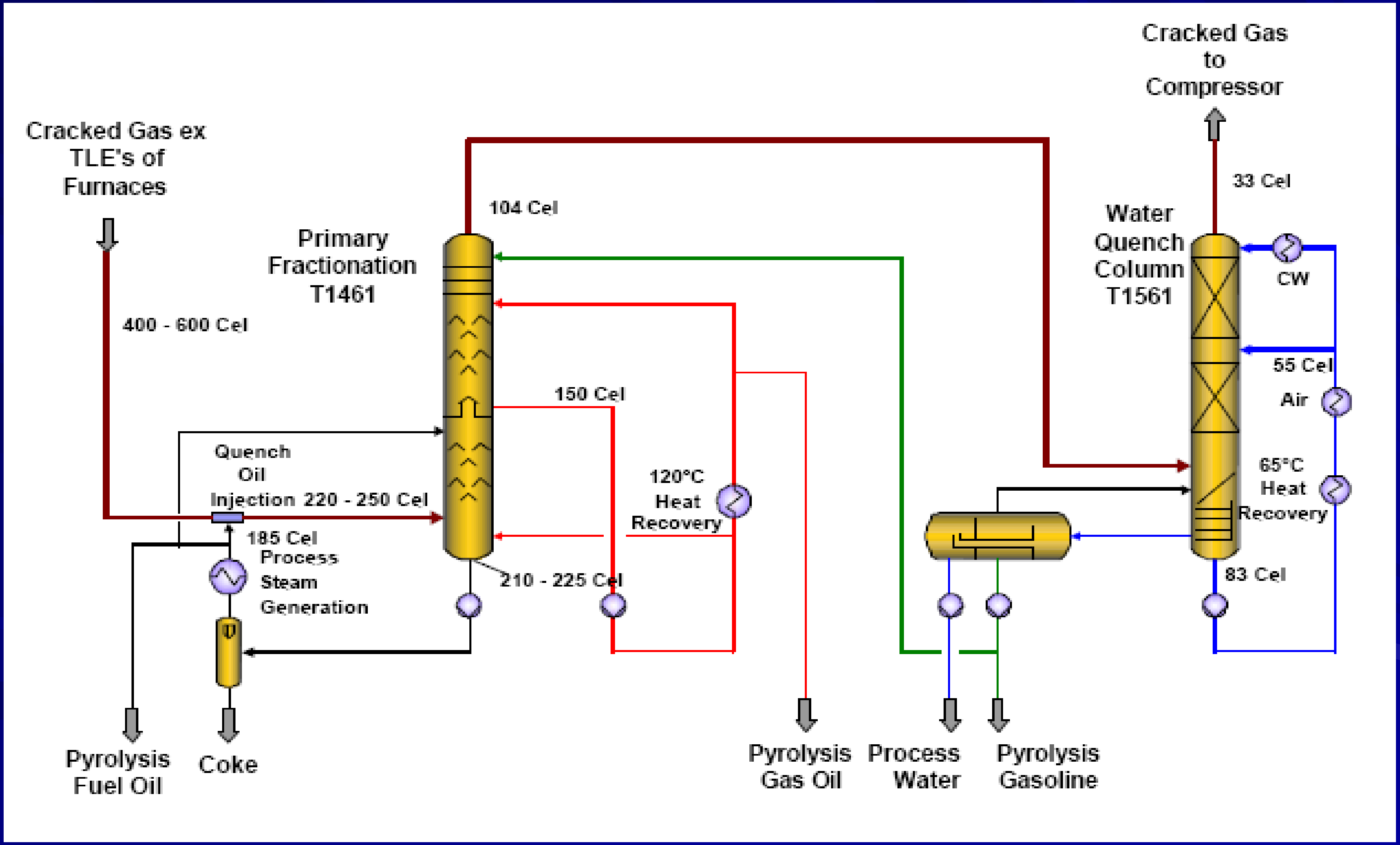
Tube arrangement in the radiant zone (Olefin-2)



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

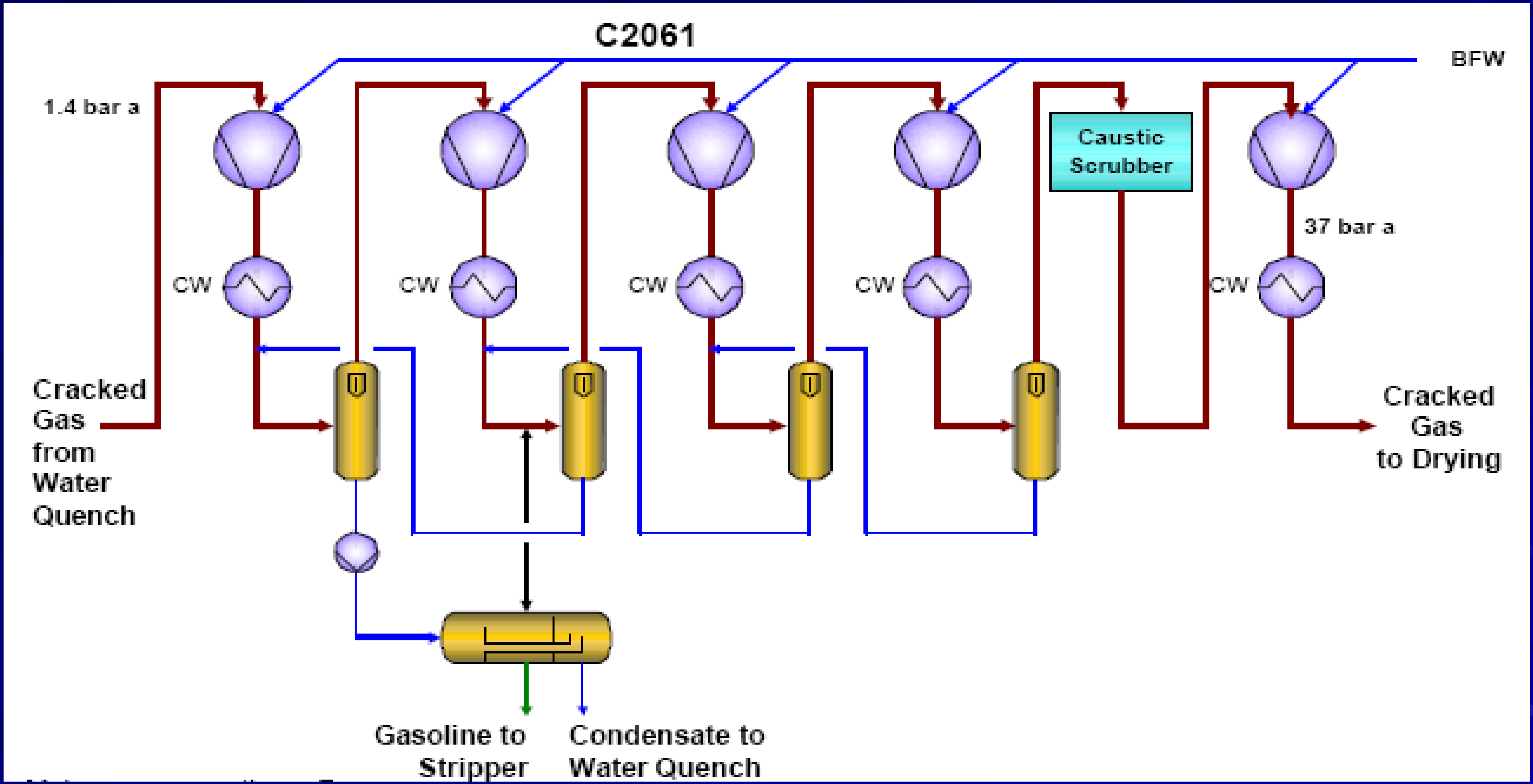
Hot section: Oil fractionating and water quench column in O-2



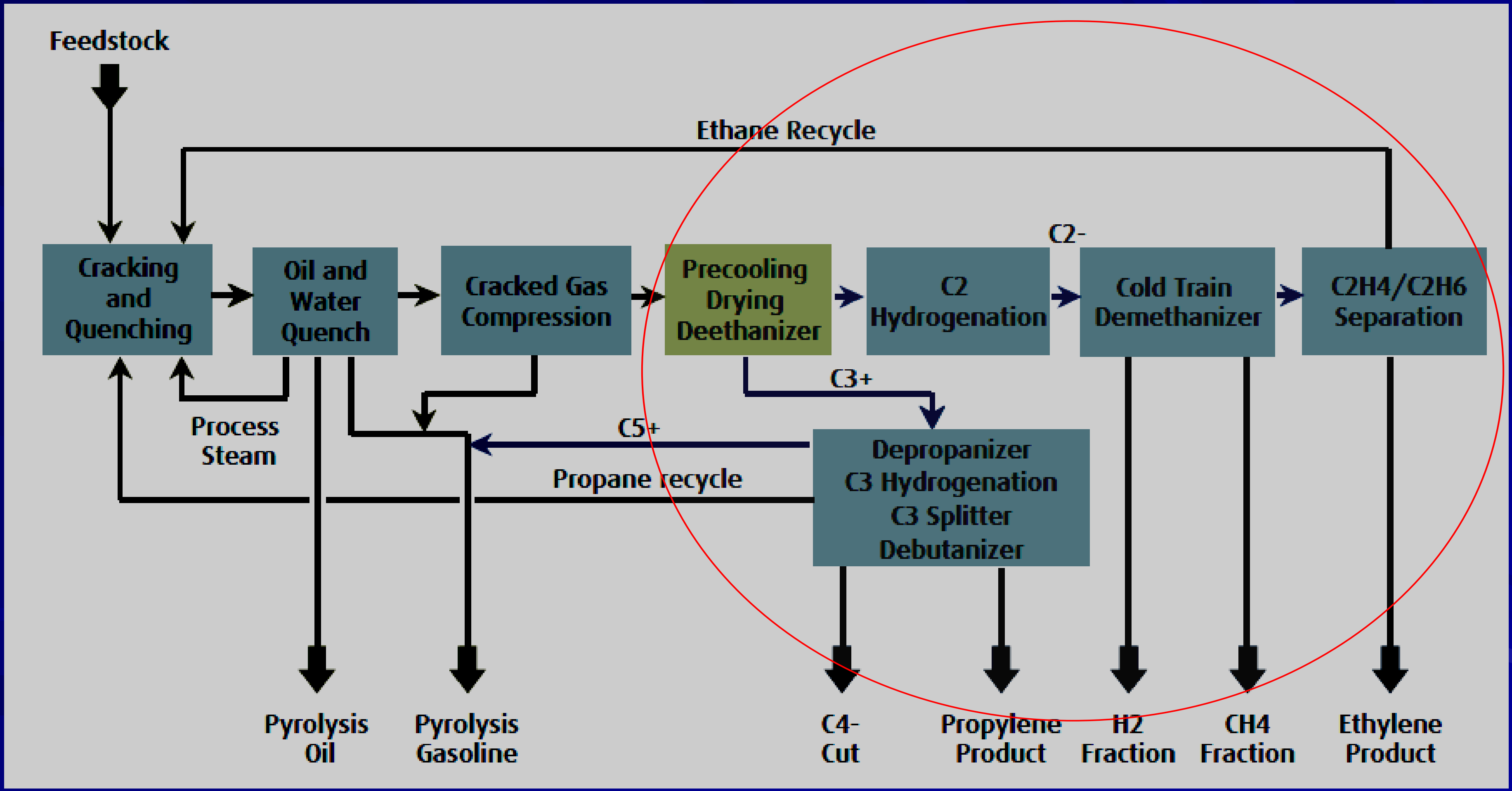
Cracked gas compression

- **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

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

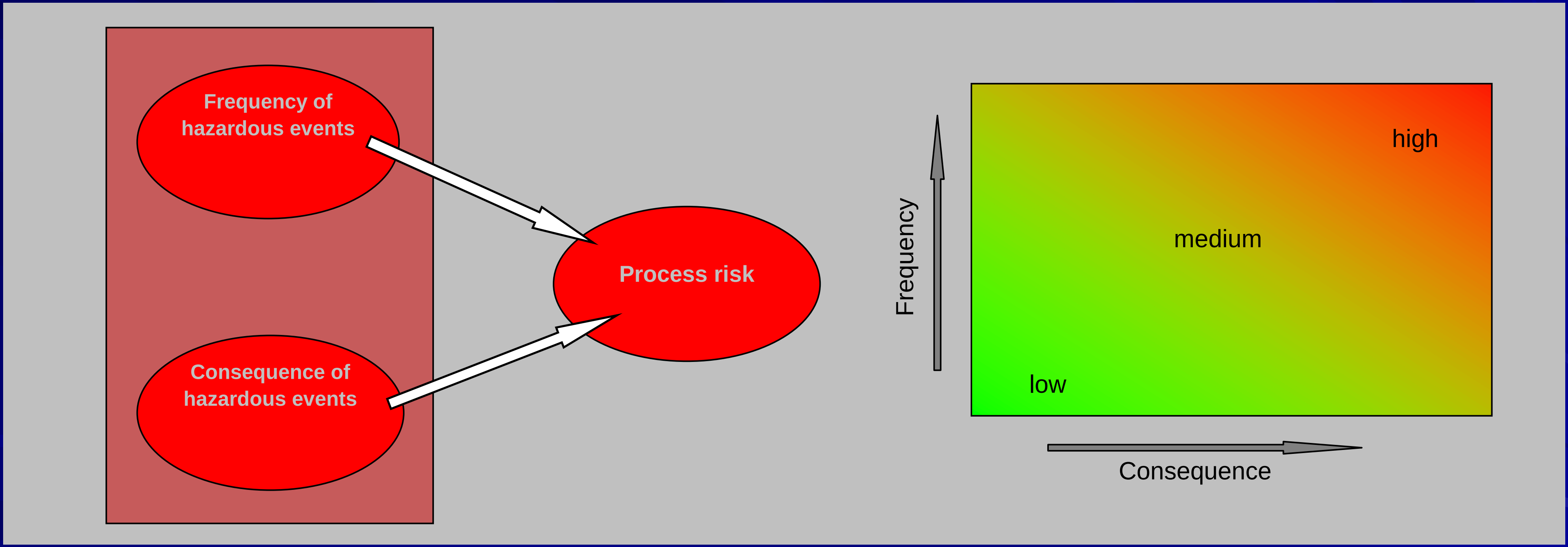
- Safety is expensive – there is nothing for free

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

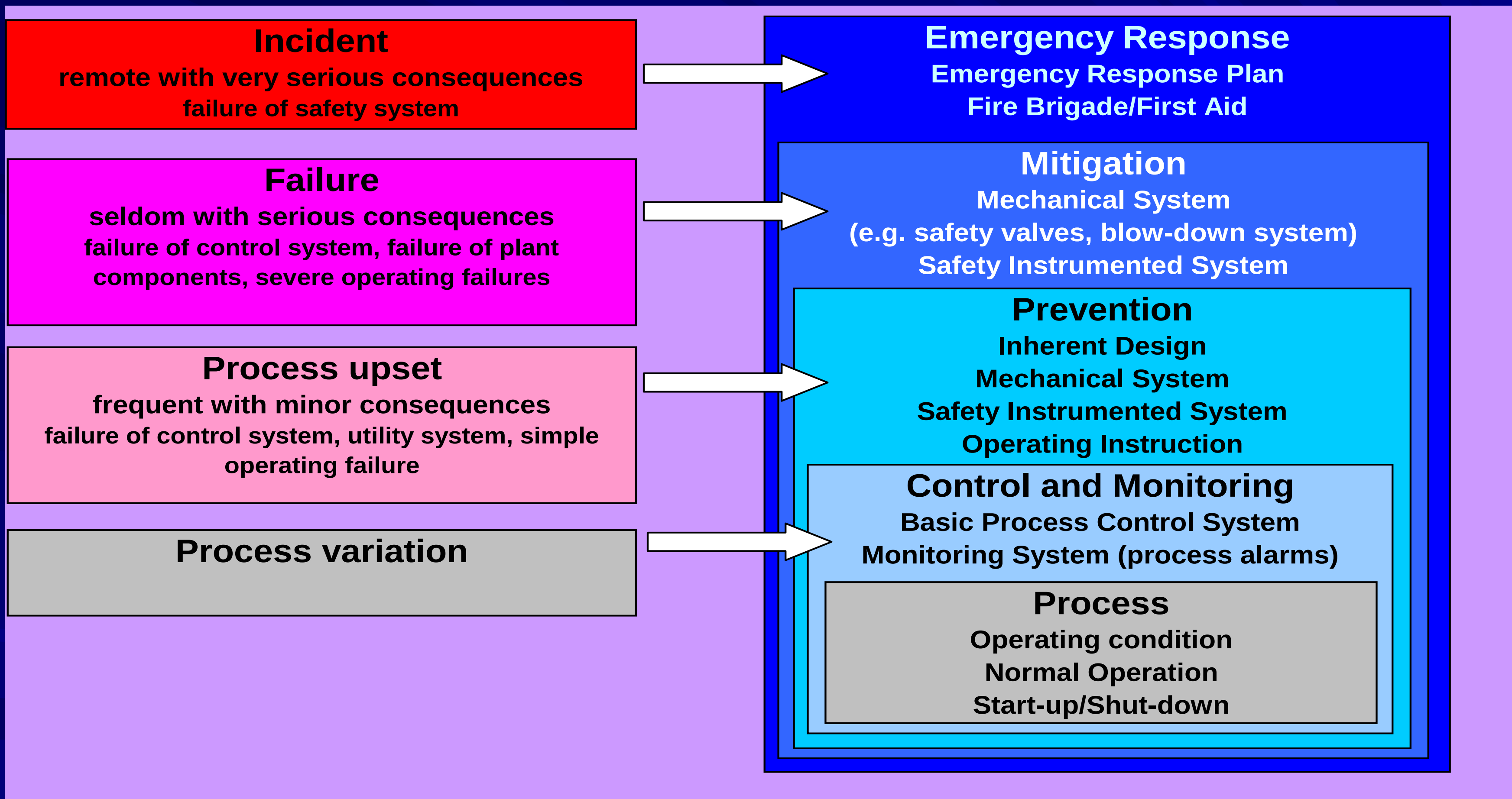
Plant safety: based on risk evaluation

- Risk consideration
- Risk matrix



Risk reduction

Levels of risk reduction measures



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

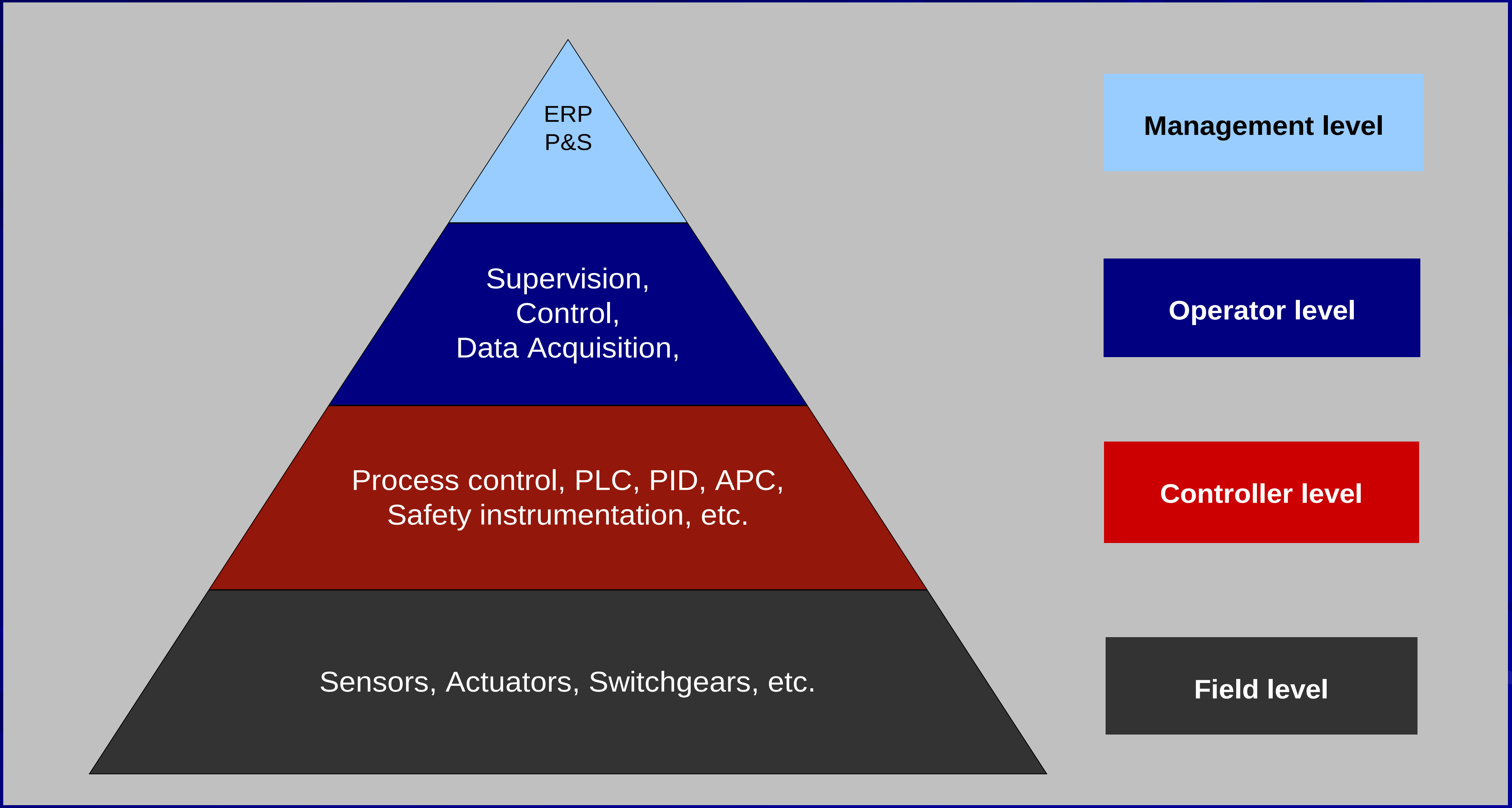
- Calculated plant lifetime: ~15-20 Years
- Nominal operation conditions:
  - Specified cases of operation
  - Design pressure and temperatures, fluid composition, flow velocity as specified
  - Start up
  - Shut down
  - Site condition

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

Process Control System	Safety Instrum. System	Fire & Gas System	PLC for P.U. & Machines	Metering System	Electrical Control System
Visualization Control process related loops	Emergency shutdown 2 out of 3 1 out of 2 SIL 1,2,3	Fire and gas detectors Alarming Deluge system	Localized control Indepen-dent	Feed and utility import Product export High accuracy	Visualization Control Switchgears, electrical consumers

Key equipment

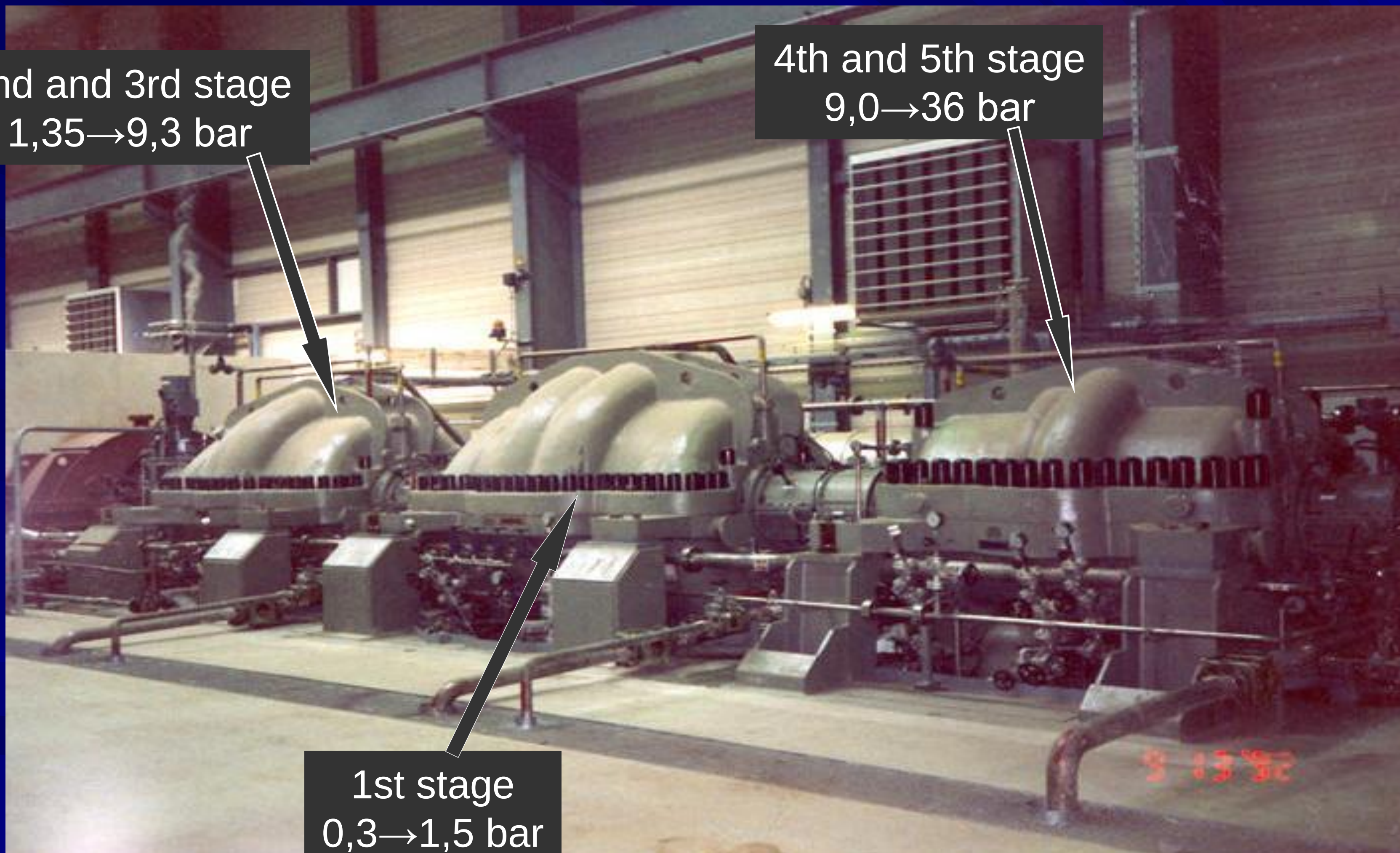
Main groups of equipment

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

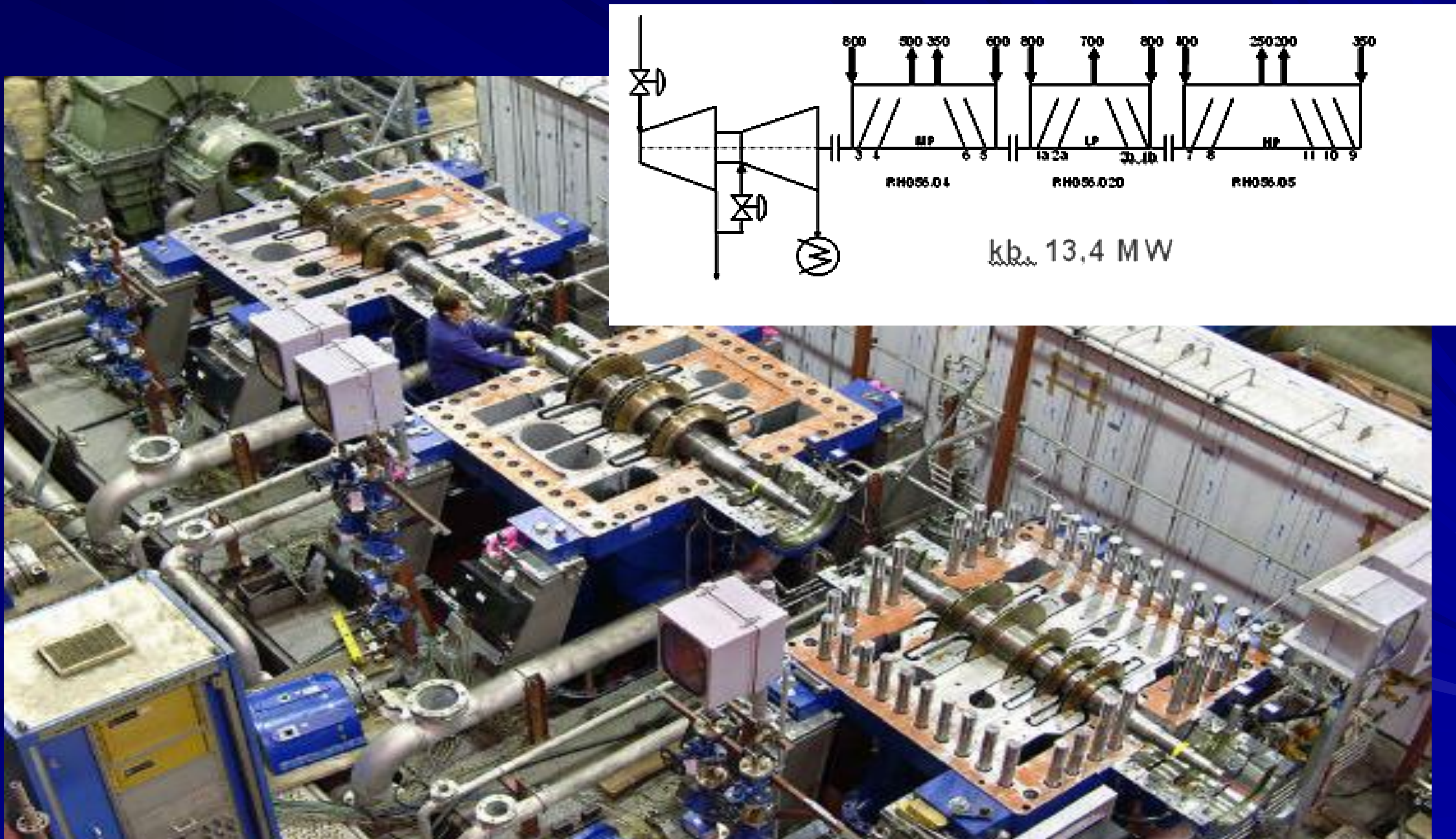
Turbo compressors in O-2 plant

- 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

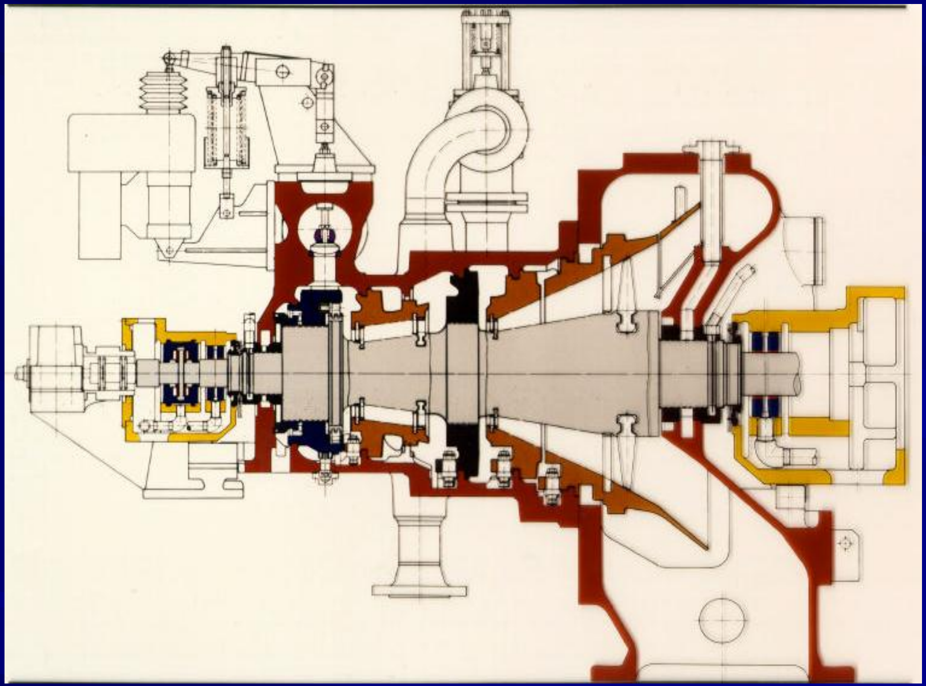


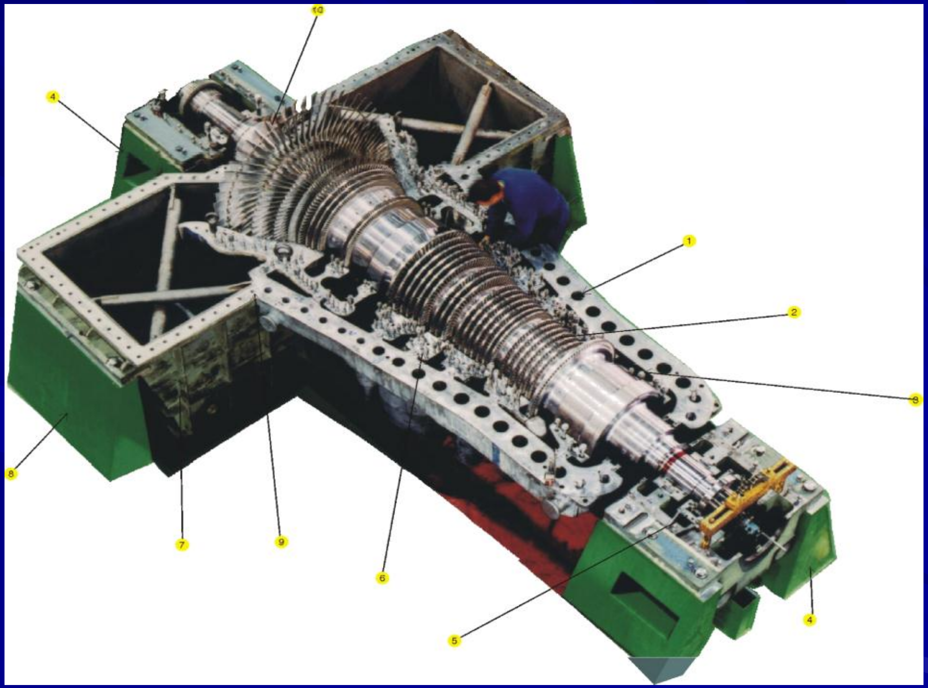
Crack gas compressor O-2 plant



Crack gas compressor LP section

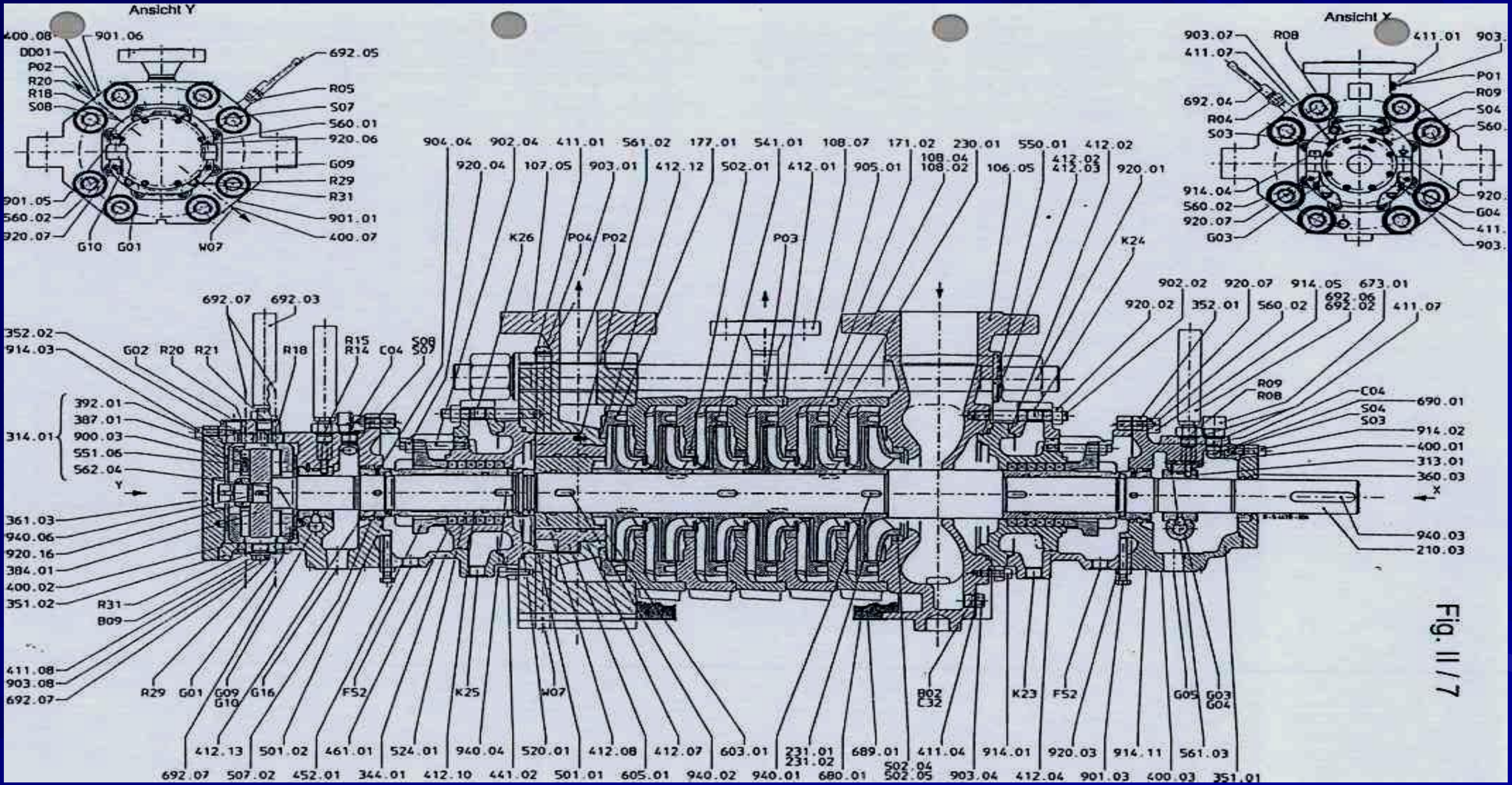
Steam turbine





Turbine driven BFW pump

Multistage BFW pump



Overview of investment and operating costs

Investment costs

Basis: WE 2010 Q1   Capacity: 800 kt

	million EUR
ISBL	704
OSBL	352
Other project cost	400
Total investment	1 456
	EUR/t Ethylene
Specific cost	1820

Ethylene production cost
Basis: WE 2010 Q1/Q2   Capacity: 800 kt

PRODUCTION COST SUMMARY	Quantity	Units	2010 Q1	2010 Q2
	(per ton)		*(€/ton)*	
Naphtha	3,230	ton	1 651,1	1 755,0
Catalyst & Chemicals			3,6	4,0
Total Raw Materials Costs			**1 655**	**1 759,0**
Fuel	0,587	ton	195,1	
High Pressure Steam (40 bar)	0,750	ton	24,1	
Cooling Water	0,454	kton	14,0	
Electricity	0,084	MWh	5,9	
Other (Utility)	0,145	-	0,3	
Total Utility Costs			**239**	**259,0**
Propylene	(0,516)	ton	(427,5)	(496,0)
Fuel (FOE)	(0,813)	ton	(270,2)	(293,0)
Benzene	(0,239)	ton	(172,9)	(201,0)
C7 - C9 cut	(0,267)	ton	(139,6)	(154,0)
Butadiene	(0,148)	ton	(137,4)	(186,0)
Other	(0,391)	ton	(214,9)	(227,0)
Total Co-Products			**(1 363)**	**(1 557,0)**
Total Variable Costs			**531**	**461,0**
Total Direct Fixed Costs			**38,8**	**38,0**
Total Allocated Fixed Costs			**31,8**	**31,0**
Total Cash Cost			**602**	**530,0**