Petchem technologies

Steam Cracking
Polymerisation

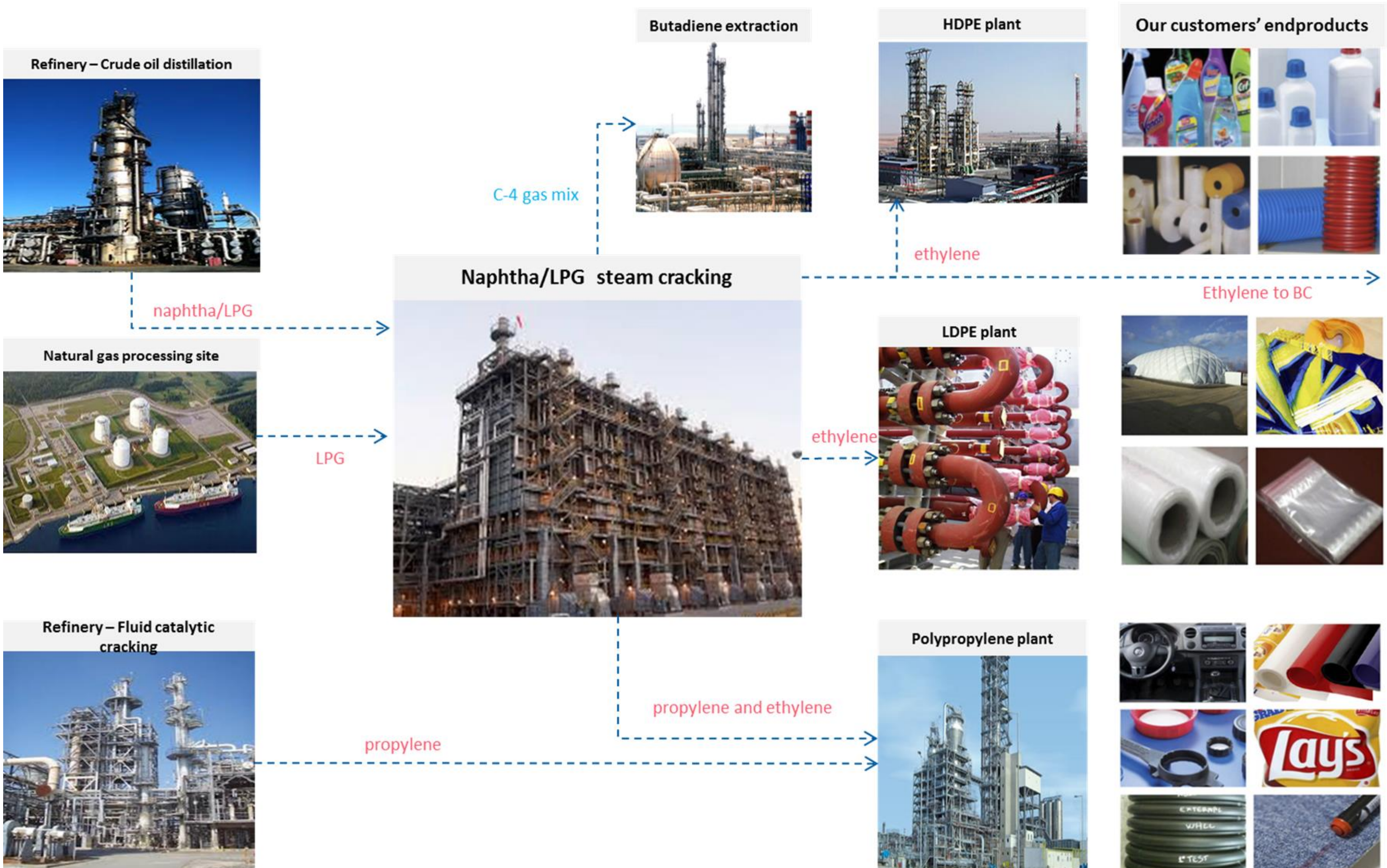
BME, Vegyészmérnöki Kar, BSc nappali tagozat

2023

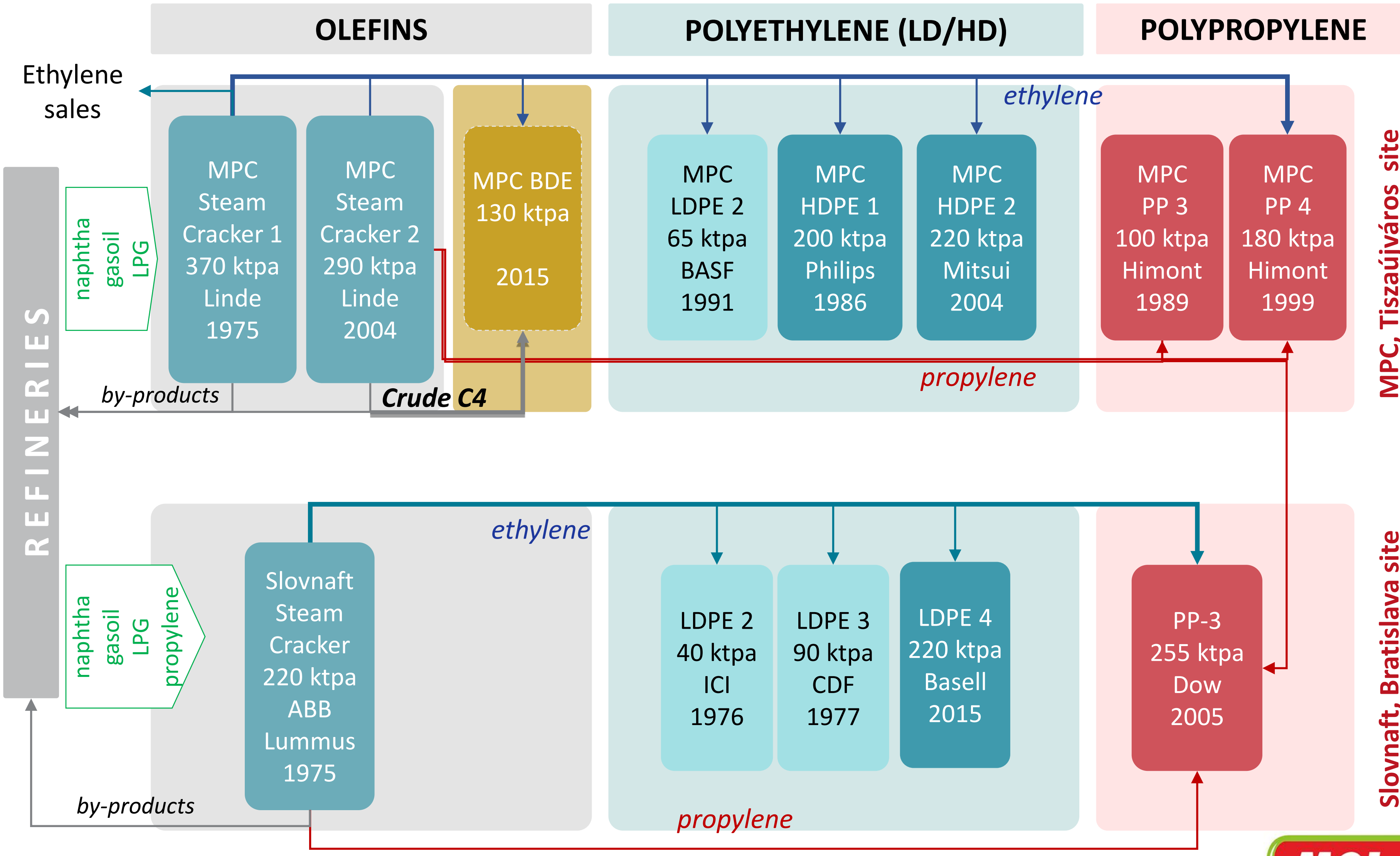
MOL PETROLKÉMIA

Slovnaft

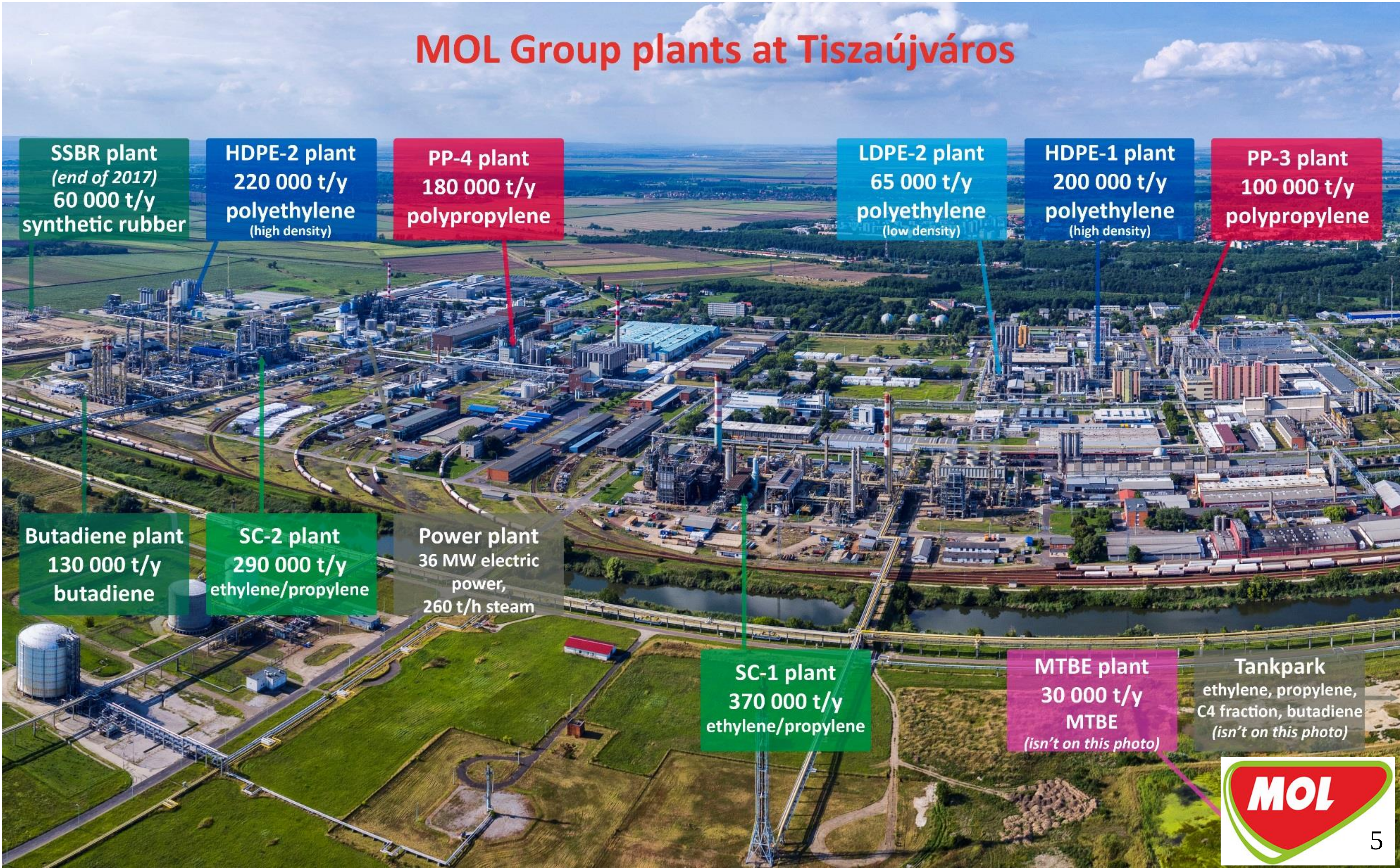
PETROCHEMICAL VALUE CHAIN



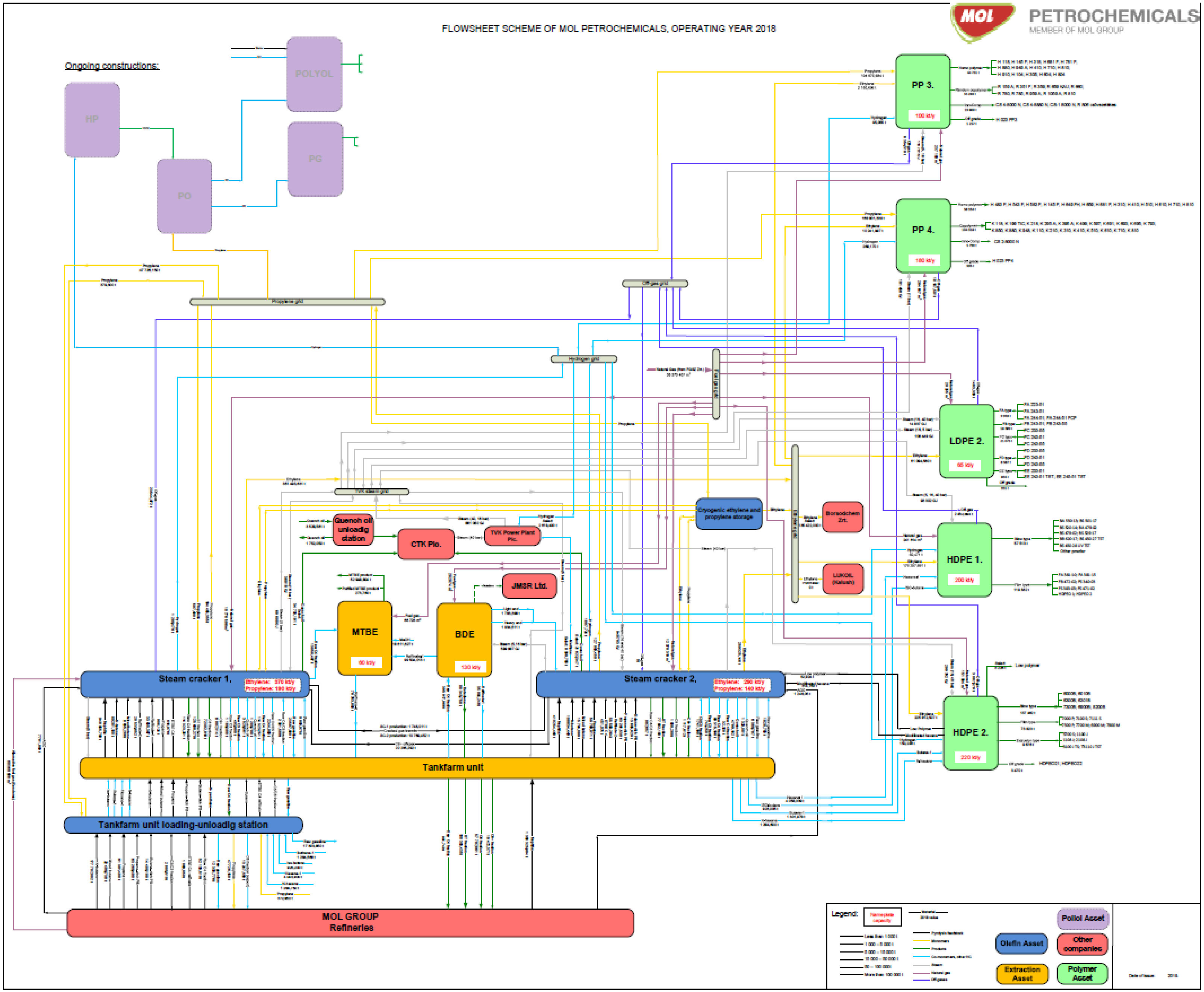
PRODUCT LINE



MPC site view



MPC flowchart

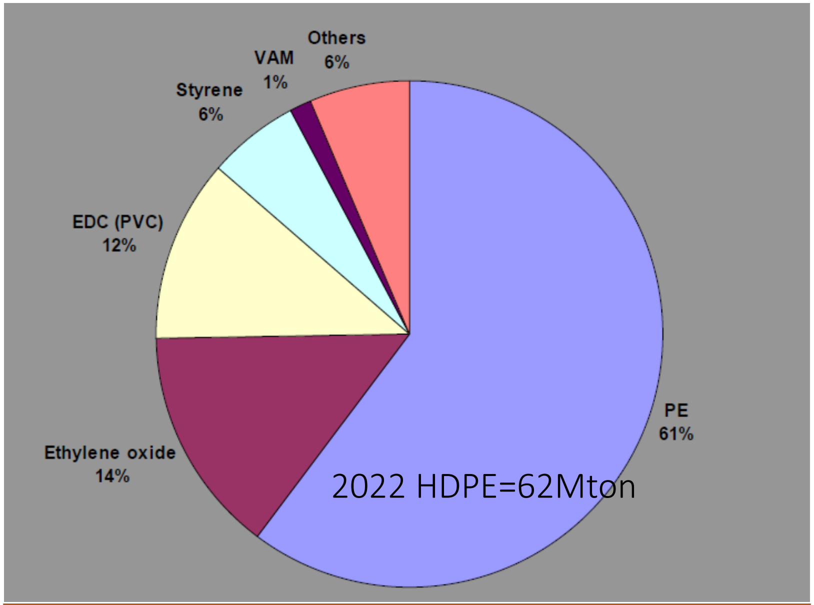


Steam Cracking technological milestones

- 1913: Standard oil's scientist patented thermal cracking process
- 1930-s Ethylene was first separated from coke owen gas and the first commercial plant for the production of ethylene was built by Linde
- 1941 Standard Jersey (former Exxon Mobil) developed the world first steam cracker at Baton Rouge
- 1950-s Ethylene emerged as a large volume intermediate replaced acethylene as a prime mateiral for synthesis
- Today ethylene is primarily produced by thermal cracking of hydrocarbons in the presence of steam, plant capacities are up to 1,5mta
- Other processes are also available or under development: ethanol dehydration 60% yield, coal to olefins by Fischer Tropsch, Oxidative coupling of methane, FCC gases=1wt%

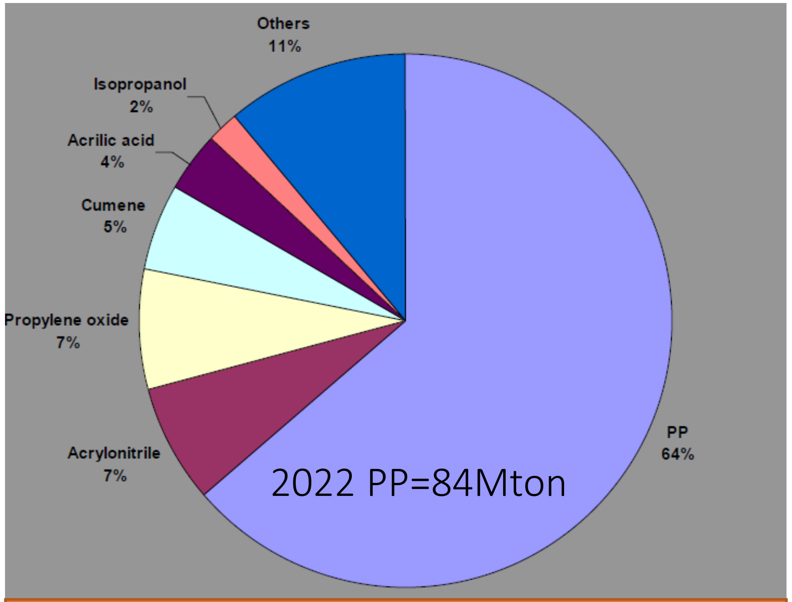
Olefin production in chemical industry

SC Feed:Ethane>**Naphtha>LPG**
Region:NE Asia>N America>Middle E>**W Eu**



Ethylene (on purpose) consumption (2009)

Techn.: **SC**>FCC>>PDH
Region:NE Asia>**W Eu**>Middle E



Propylene consumption (2009)

Olefin production principles

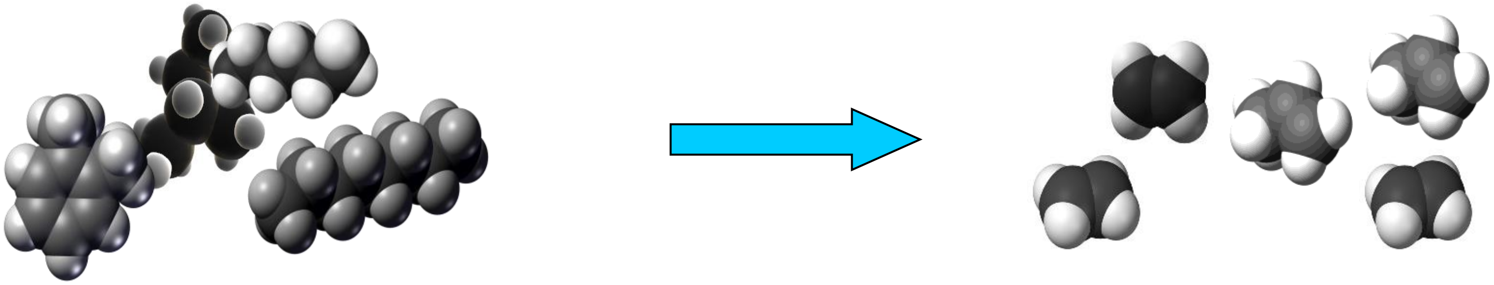
- Main products are 2, 3 carbon number molecules, C2-3 yield is feedstock dependant

- Chemical bond energy C-C < C-H < C=C < C≡C , energy intensive process

- Feedstock: LPG, virgin naphtha, atmospheric gasoil
- Products: propylene, ethylene

- Byproducts: hydrogen, methane, fuel oil, pyrolysis gasoil, pyro gasoline, benzene, toluene, raw C4- fraction, coke (in the furnaces much more unwanted molecules are forming but these are transformed into valuables e.g. acetylene→ethylene)

- Thermal cracking in a high alloy tube sheet in the presence of water, residence time <1sec. Long mainly parrafinic carbon chains break into smaller ones with hydrogen elimination various rearrangement and recombination reactions are also take place between the free radicals



Chemical reactions

Thermal cracking is an equlibrium reaction affected by furnace geometry, T, P, Steam presence of contaminants, catalytic effect of furnace tube metals

Primary reactions:
Radical formation as a result of breakage of long saturated carbon chains
Secondary reactions:
Coke & CO2 formation
Other reactions:
Condensation reactions to form e.g. benzene

~3000parallel reaction is happening, depending on feedstock

Modeling is done by SPYRO software

Chain Start, C-H or C-C bond scission

$$C_2H_6 \rightarrow CH_3\cdot + CH_3\cdot$$

Chain transfer:

$$CH_3\cdot + C_2H_6 \rightarrow CH_4 + C_2H_5\cdot$$

$$C_2H_5\cdot \rightarrow C_2H_4 + H\cdot$$

$$H\cdot + C_2H_6 \rightarrow H_2 + C_2H_5\cdot$$

Chain termination, radical recombination:

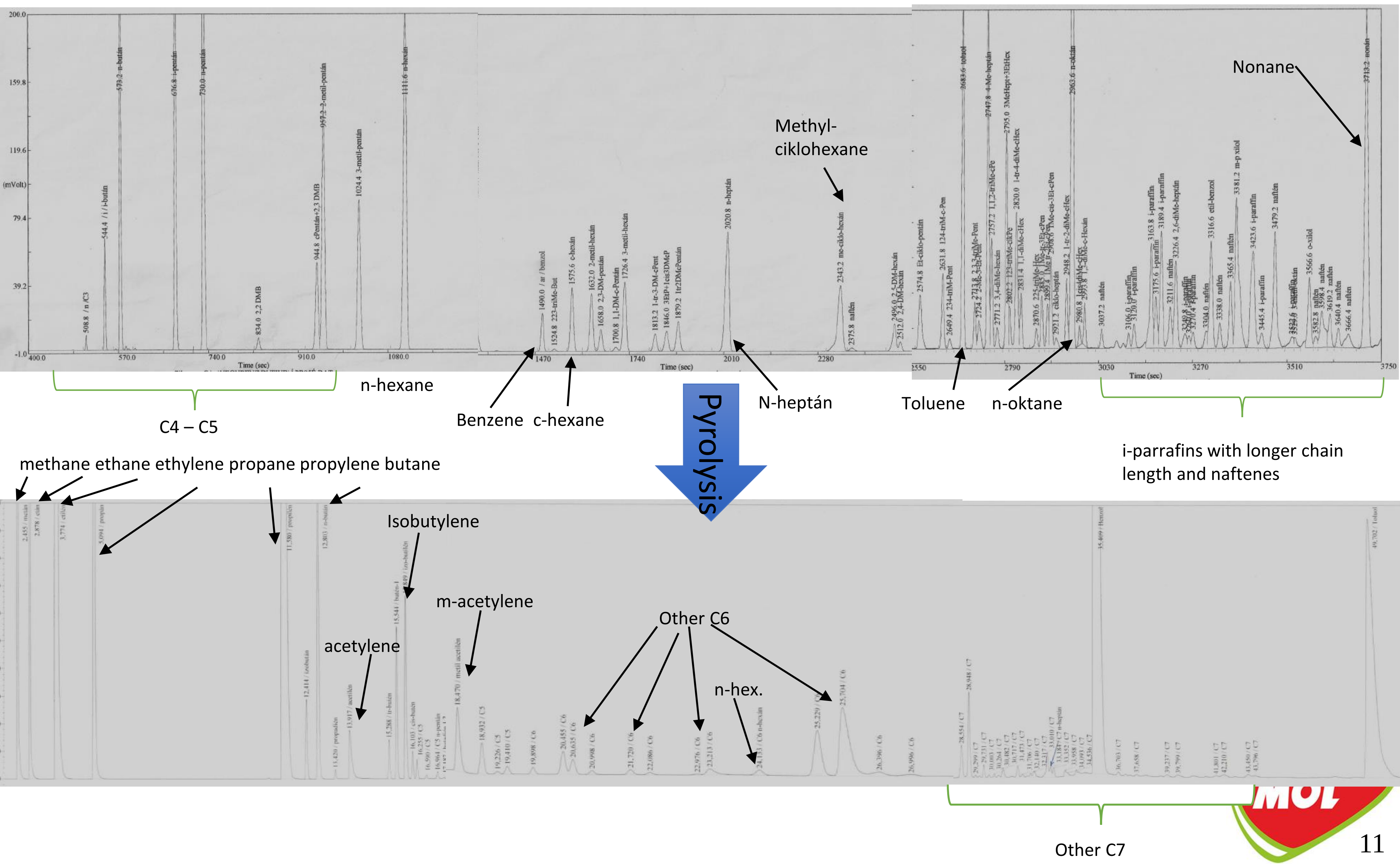
$$H\cdot + H\cdot \rightarrow H_2$$

$$CH_3\cdot + C_2H_5\cdot \rightarrow C_3H_8$$

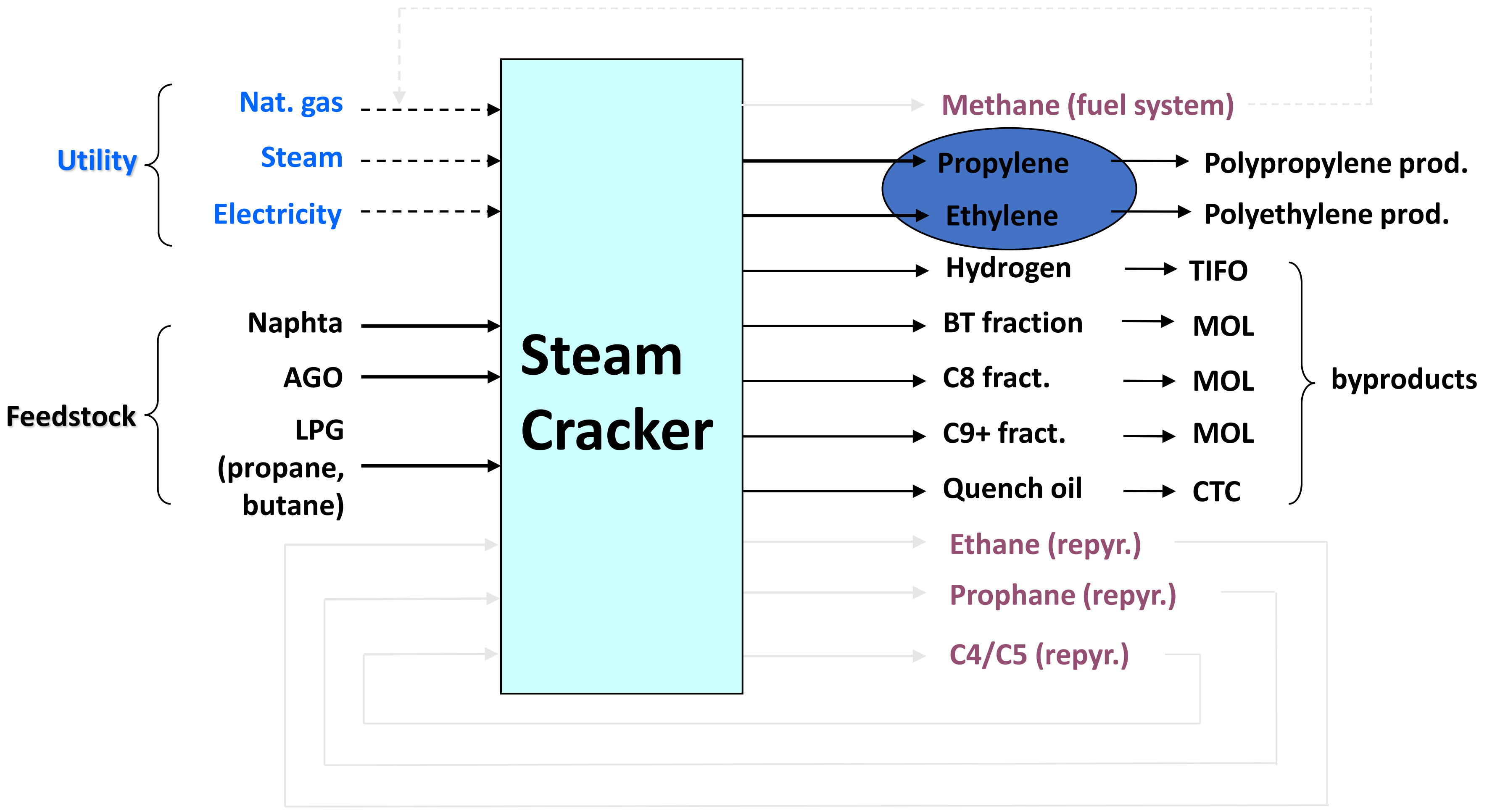
Molecule addition, ring formation:

$$C_2H_4 + C_4H_6 \rightarrow C_6H_6$$

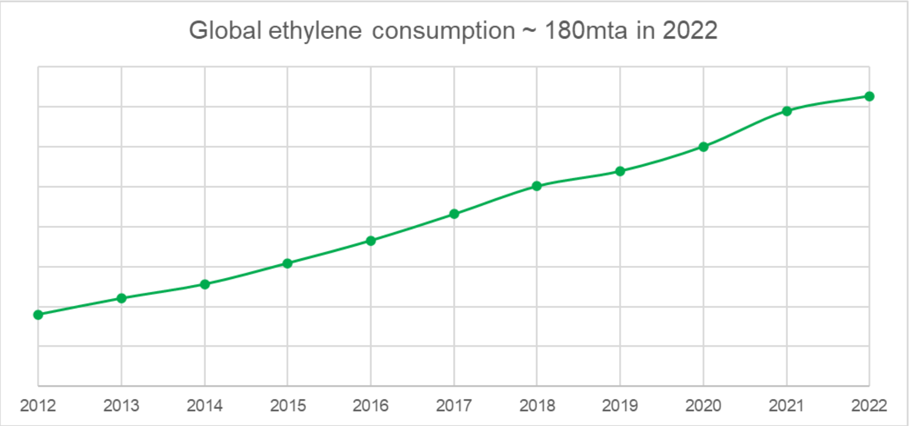
Cromatograph of virgin naphtha and pyrogas

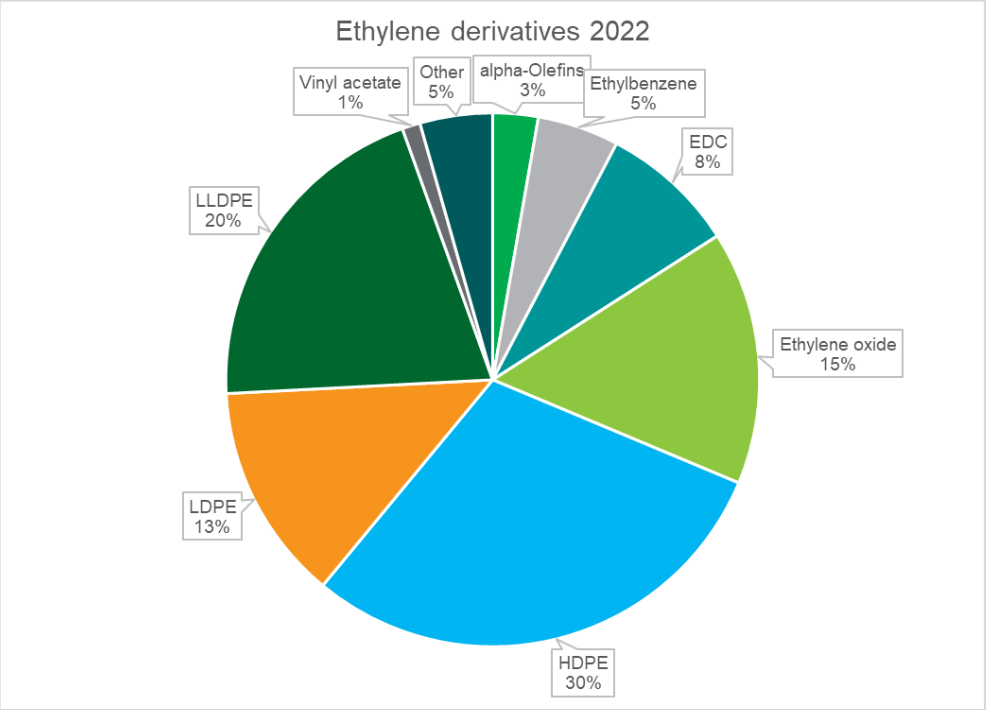


SC block scheme



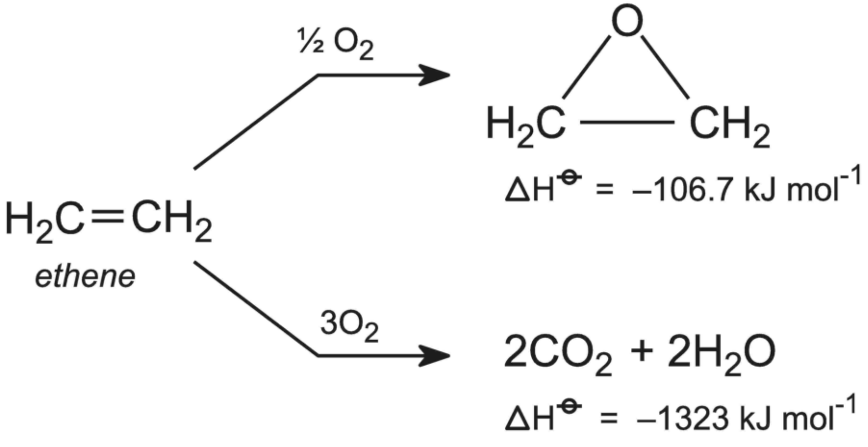
Ethylene derivatives

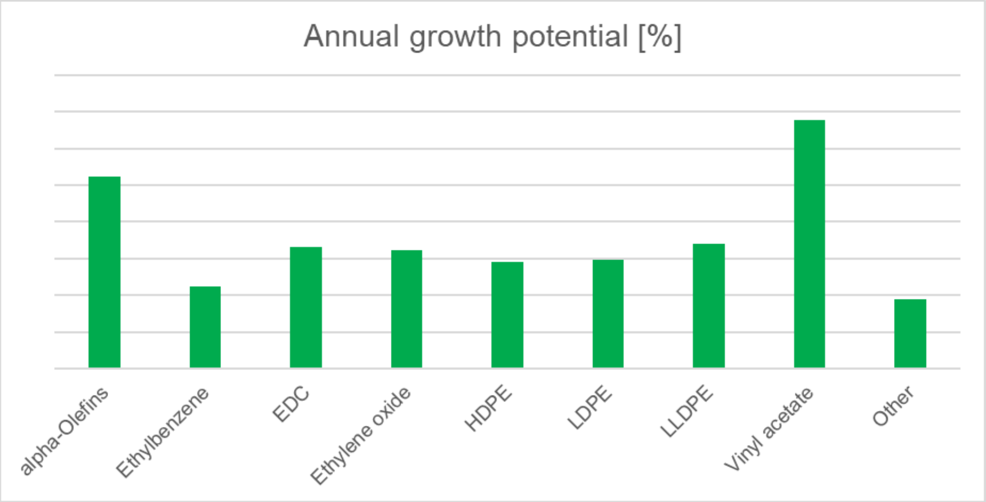




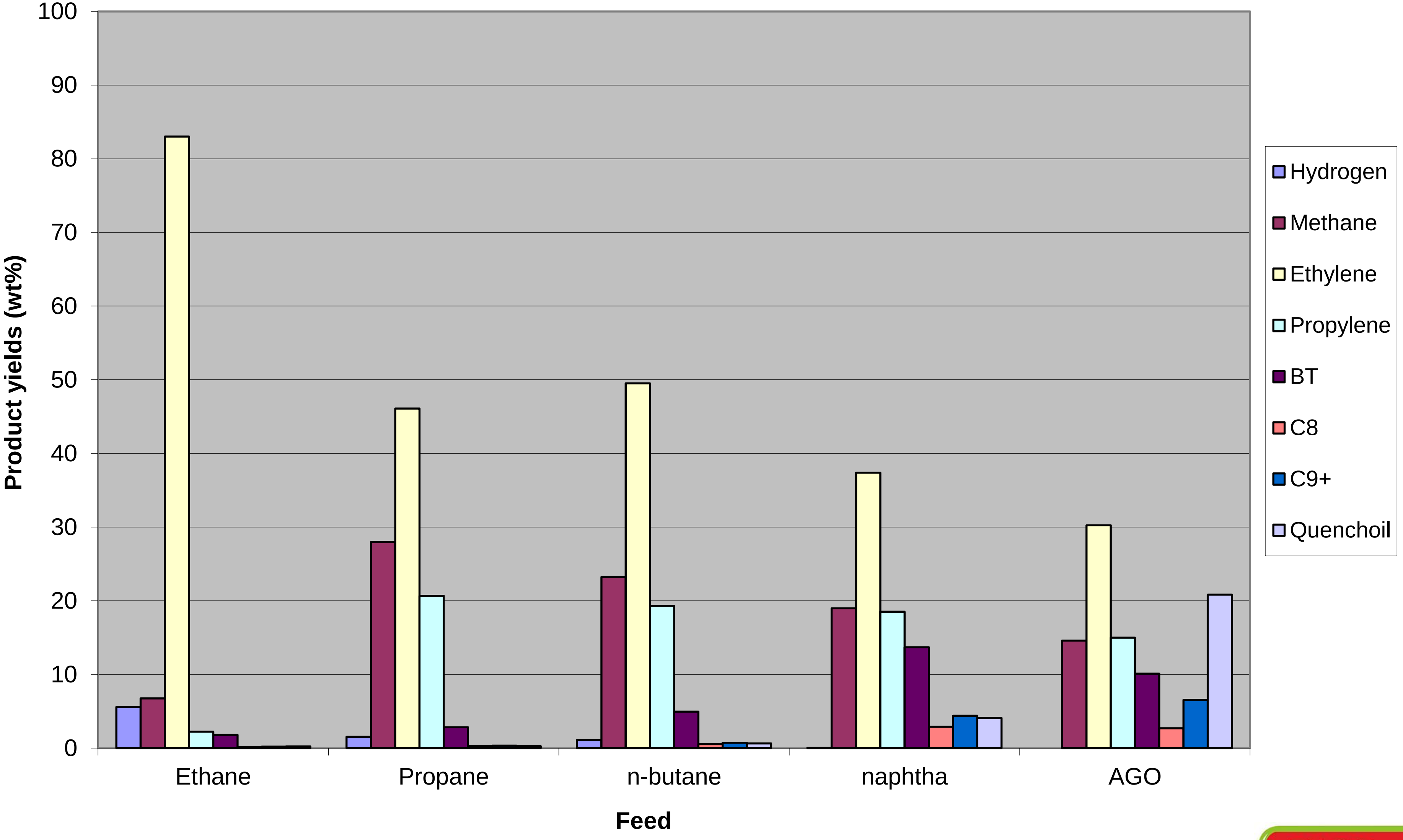
Consumption in WE + CE ~ 20mta

NE Asia > N America > Middle E > W E >> C E 2mta





Feedstock VS Yield



Comparison of ethane and naphtha crackers

	Ethane	Naphtha
SEC (GJ/t ethylene)[a]	17–21 (typical) and 15–25 (maximum)	26–31 (typical) and 20–40 (maximum)
SEC (GJ/t HVCs)	16–19 (typical)	14–17 (typical)
CO_2 emission (t CO_2/t ethylene)[b]	1.0–1.2 (typical)	1.8–2.0 (typical)
CO_2 emission (t CO_2/t HVCs)	1.0–1.2	1.6–1.8
Ethylene yield (wt%)[c]	80–84	29–34 (30% typical)
Propylene yield (wt%)	1–1.6	13–16
Butadiene yield (wt%)	1–1.4	4–5
Aromatics and C4+ yield (wt%)	2–3	10–16
HVCs yield (wt%)	82 (typical)	55 (typical)
Methane yield (not counted as HVCs) (wt%)	4.2	13–14
Hydrogen yield (not counted as HVCs) (wt%)	4.3	1
Backflows to refinery (not counted as HVCs) (wt%)	0	9–10
Losses (due to fouling, coking, etc.) (wt%)	1–2	1–2

[a] Energy use is based on [19,21]. SEC here only refers to process energy use in pyrolysis and separation.

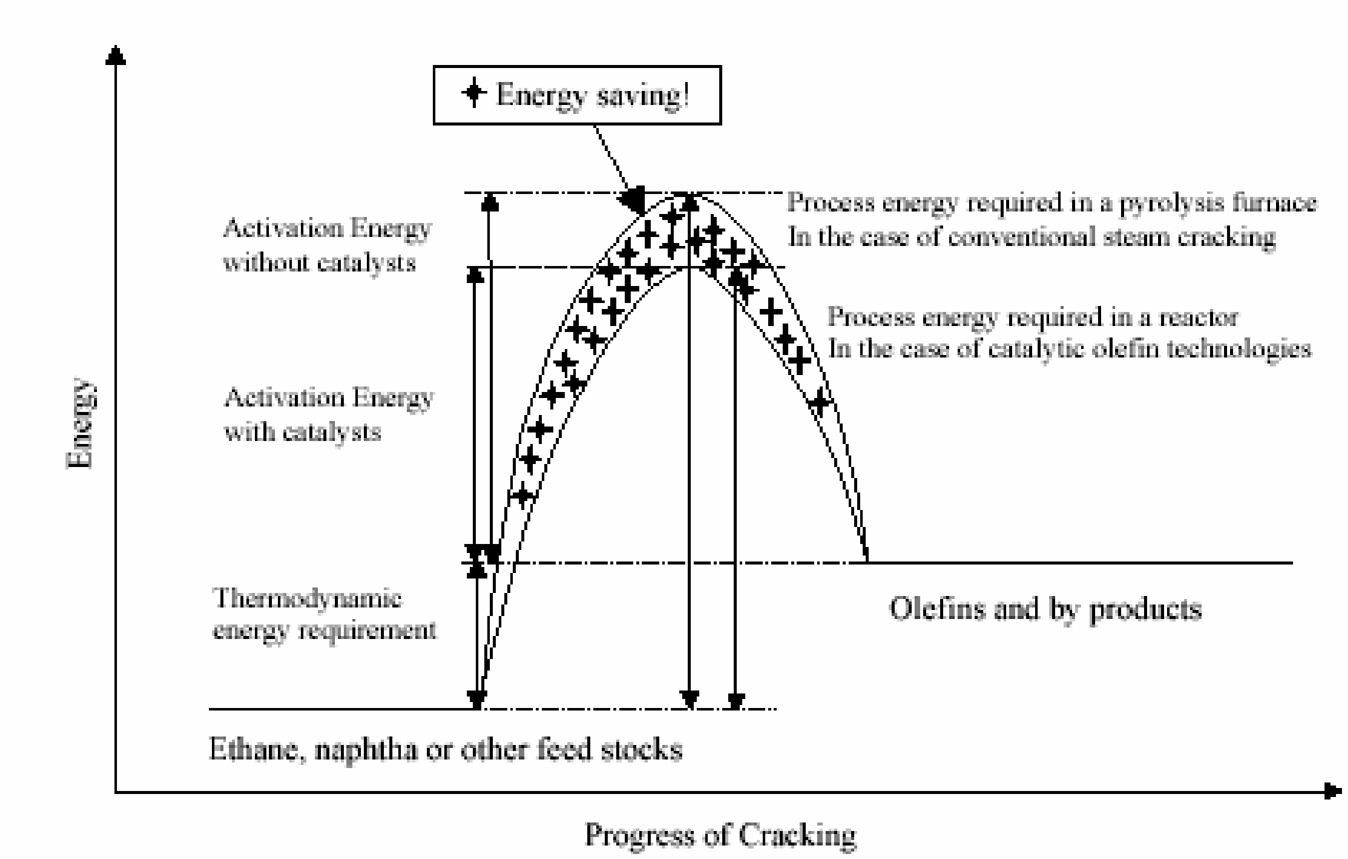
[b] Emissions are calculated based on [21,67]. Emissions are the result of fuel combustion and utilities, both of which use fossil fuel. Ethane cracking results in higher hydrogen and ethylene content, therefore less CO_2 emission per ton of ethylene, than naphtha cracking does.

[c] Yield data is based on [21,22]. Yields are on mass basis and are all final yields.

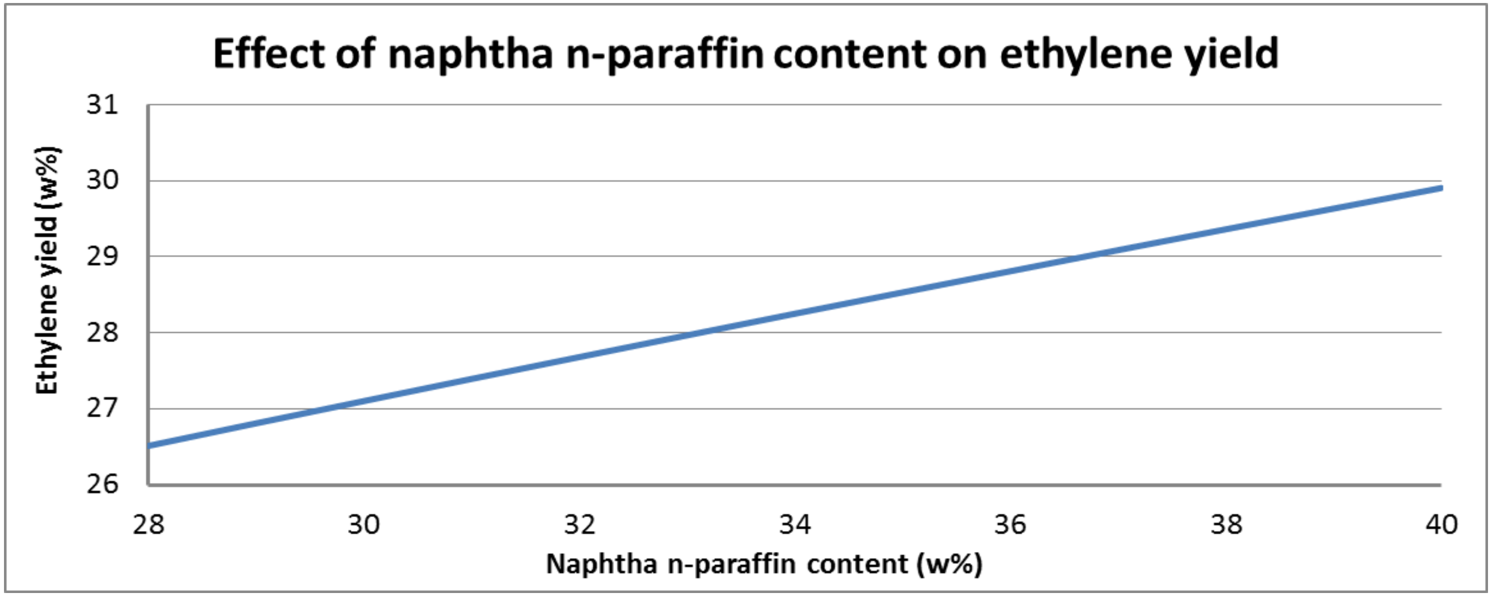
Long term profitability depends on energy prices

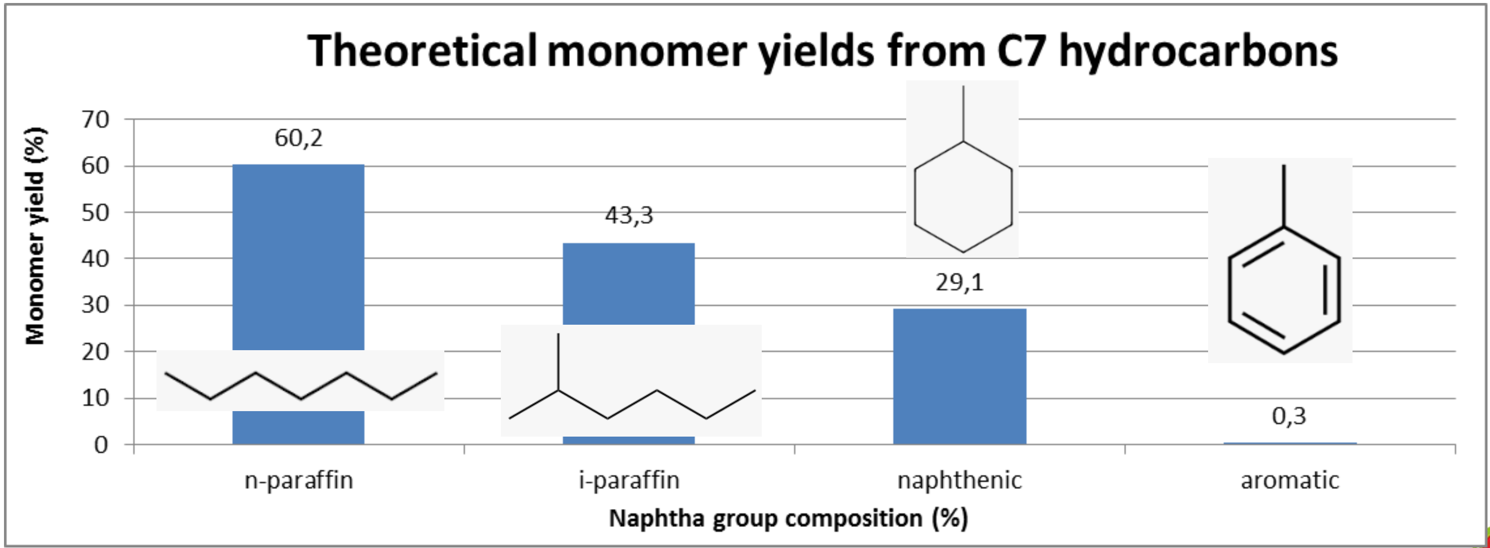
Heat integration increases CAPEX and adds to complexity

Future improvement: Energy-saving opportunity



Ethylene yield as a function of n-paraffin content





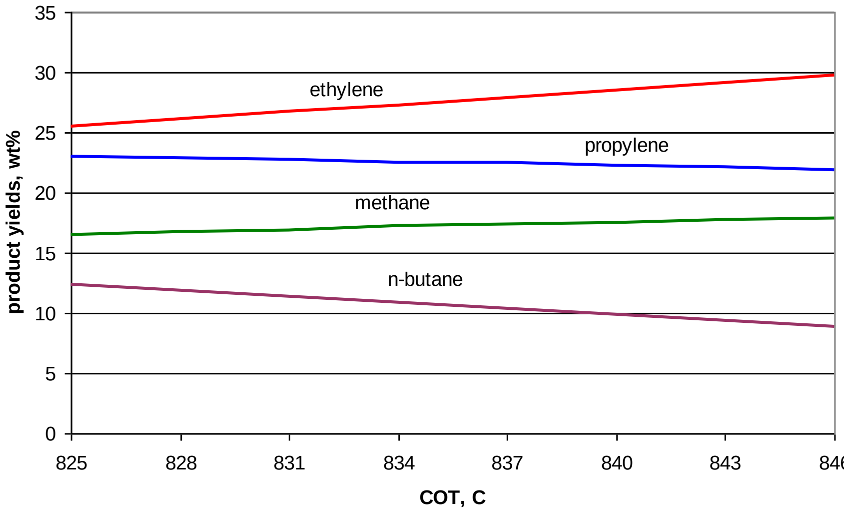
Cost to make ethylene from different feeds: ethane < propane < naphtha < gasoil

Parameters affecting monomer yield

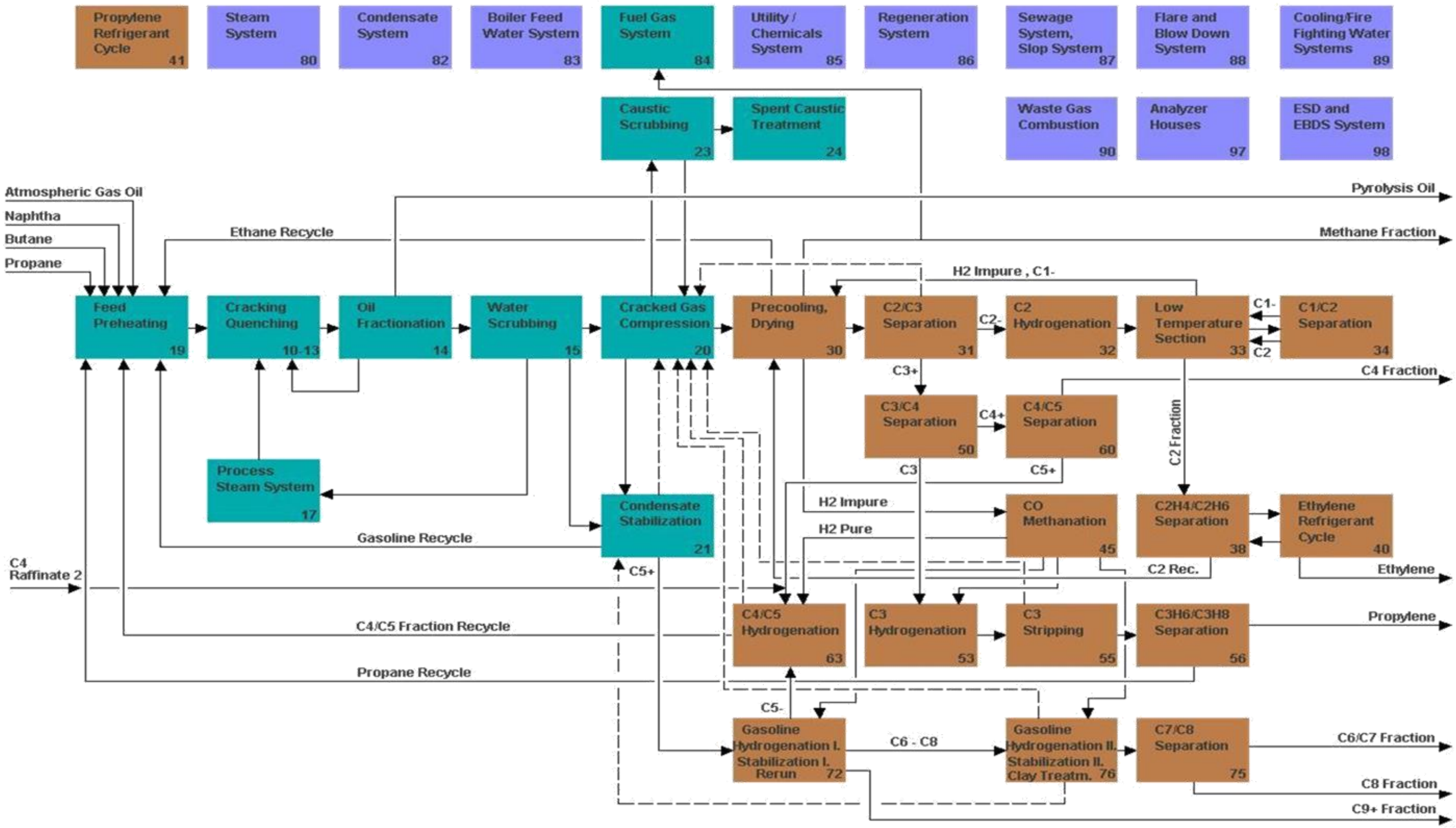
- Feedstock, paraffin rich is the best. MPC spec:

Total N-paraffin	min.27 %
Total paraffin	min.63 %
Naftenes	max.27 %
Aromatics	max. 12 %

- Lower carbon number chains yields more ethylene
- Furnace residence time 0,1-0,5sec, shorter favors primary monomer forming reactions
- High furnace pressure favors secondary reactions, optimal = 2-3barg
- Diluting steam reduces partial pressure supress secondary reactions, prevents excessive coke formation C + H2O = CO + H2, heavy feedstocks needs more steam
- Higher furnace temperature favors the formation of ethylene, low temperature favors oligomerisation, fast heating up favors monomer formation, heavy feedstock requires lower cracking temperature. Optimum=800-850°C



SC2 block diagram

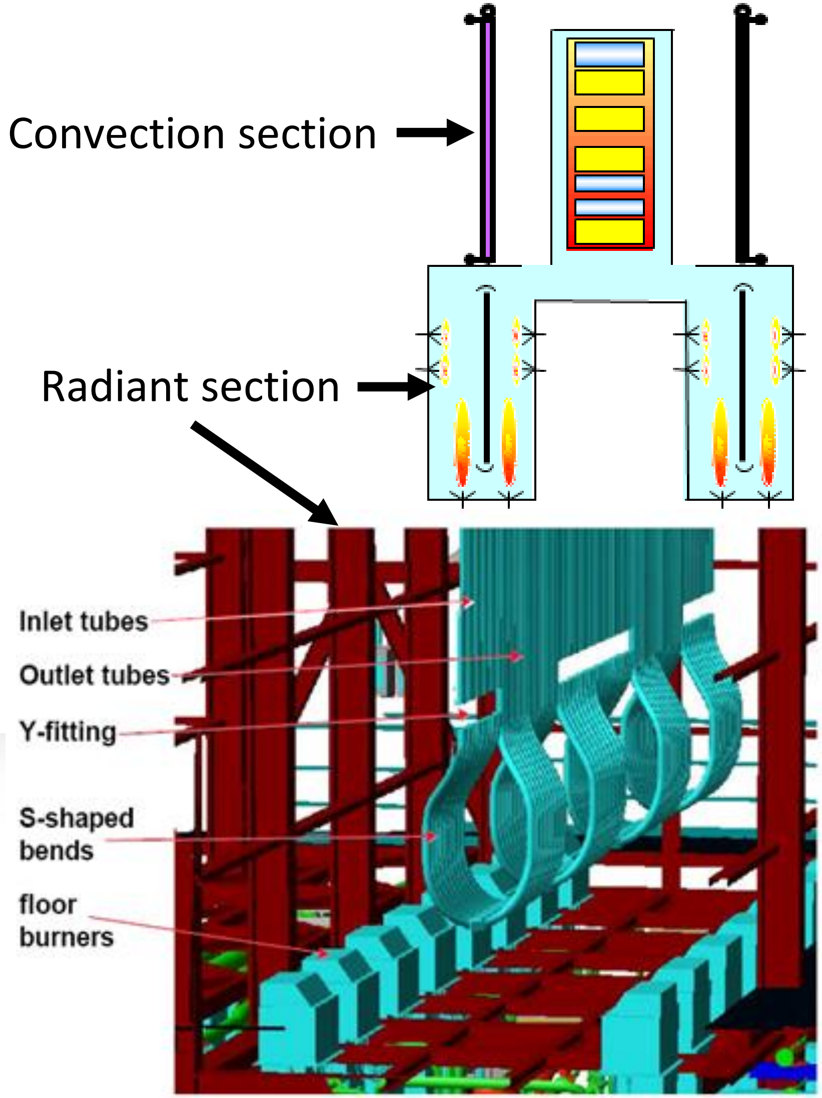


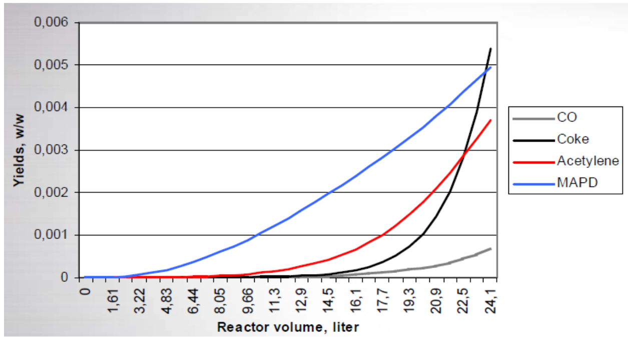
Cracking furnaces (SC1=11pcs SC2=4pcs)

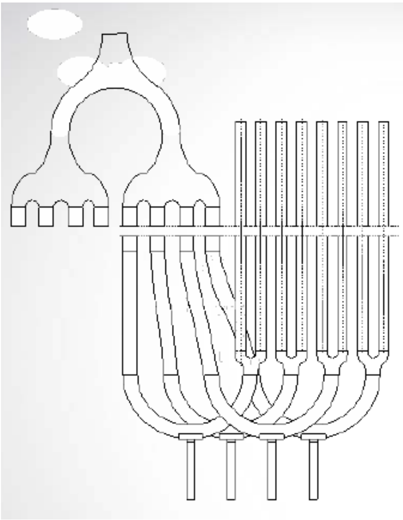
- **Convection zone** feeds mixes with diluting steam then waste heat preheats the mixture before the radiation zone
- **Quneching & steam generation** hot pyrogas is cooled, heat is utilised to drive steam turbines

- **Radiation zone** primary and secondary reactions
- **Burners** are installed into the furnaces to provide necessary energy to the radiation zone by burning natural gas, methane and hydrogen from pyrolysis gas

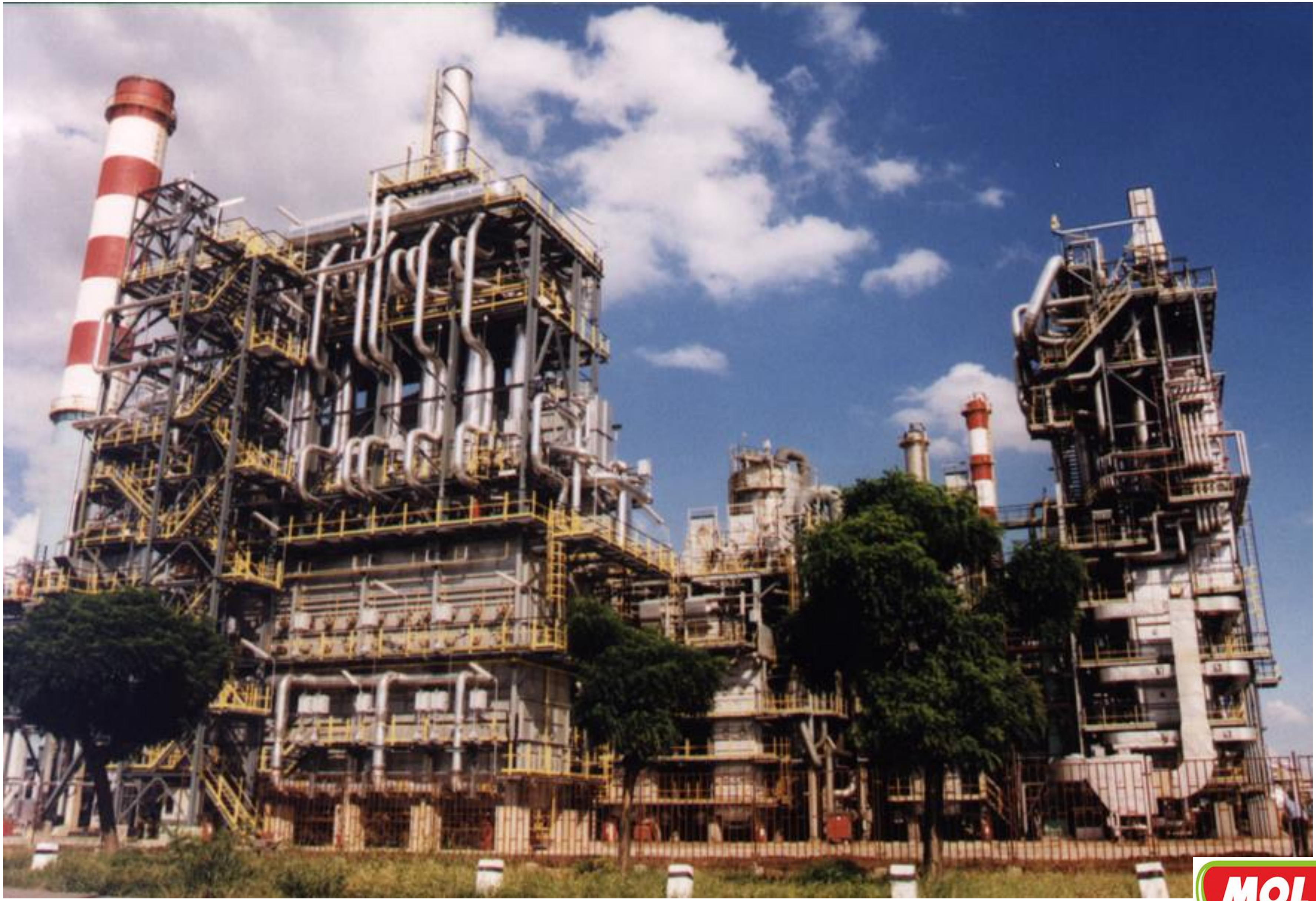
- By products:





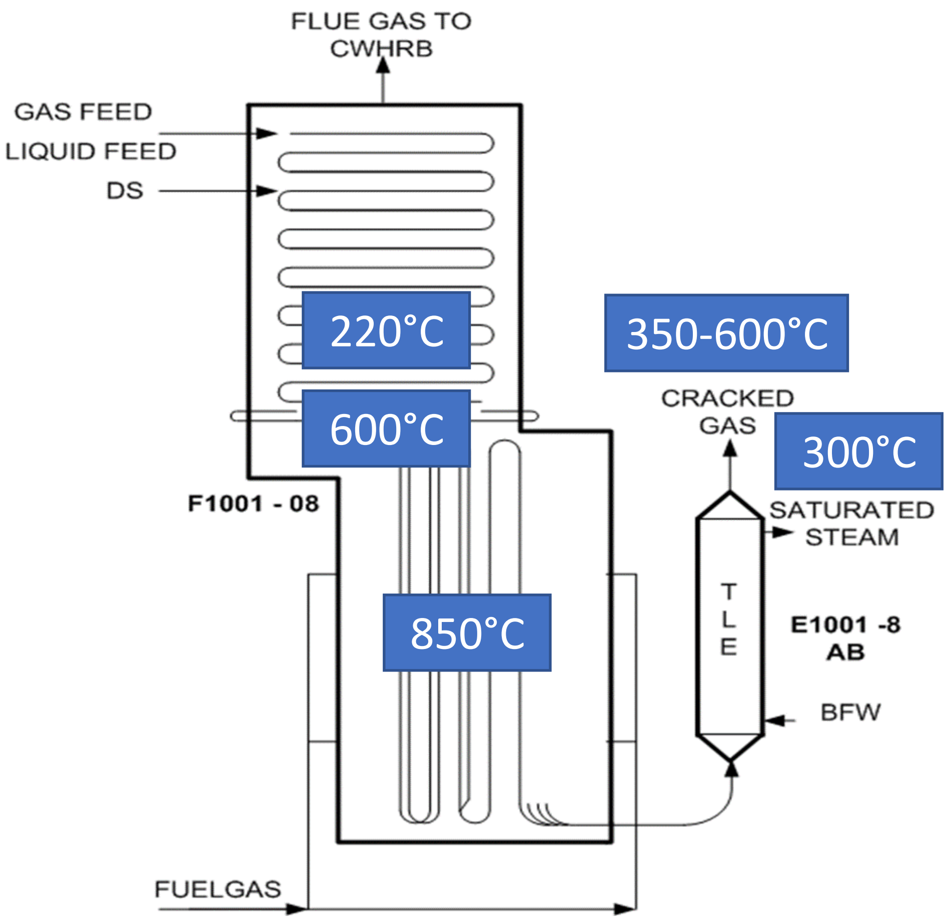


Furnaces in SC1



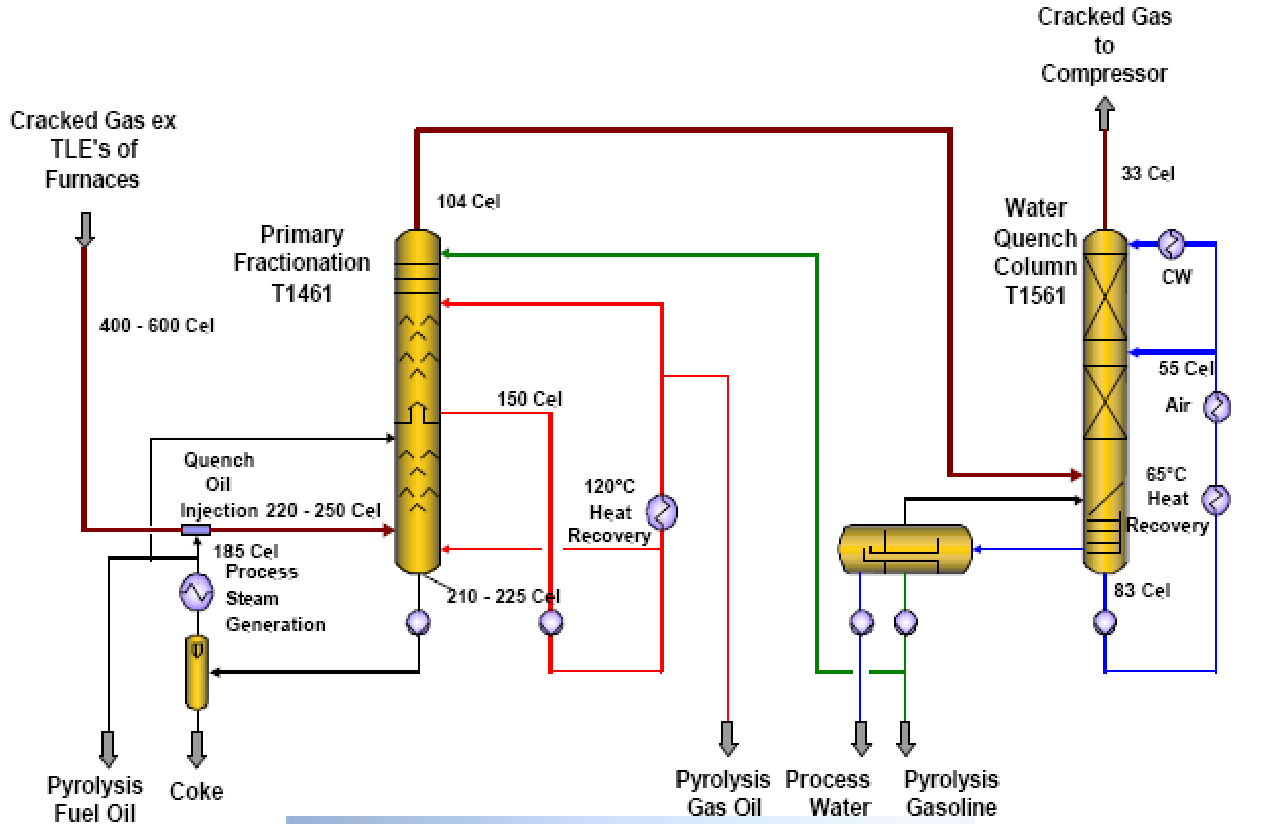
Pyrogas cooling (quenching) SC1

- Quick cooling to avoid side reactions by means of tube sheet quench coolers, saturated steam is generatated @ 110barg in the shell
- BFW is deionised and has sufficient pressure for steam generation
- Pygas outlet temperature depends on run time
- Pygas is furter cooledto 180°C with direct quench oil injection, quench oil -a tar like liquid with high aromatic content- is a product of pyrolysis
- Pygas is collected from all furnaces then led into the oil washer column



Primary fractionation and water wash column in SC2

- Pygas is further cooled with quench oil injection
- 2 quench oil cycles is used (Pyrolysis Fuel Oil and Pyrolysis Gas Oil) to remove/utilise the heat from the Pygas. Both cycles are utilizing the heavy fraction of Pygas
- Quench oil can be used for:
  - carbon black manufacturing
  - can be sold as fuel oil
  - Quenching and heat transfer purposes in the SC technology
- Top product of the first column is Pygas and steam @ 104°C goes to the water wash column where waste heat is recovered, pyro gasoline and steam is condensed together by means of water
- H2S in the Pygas is neutralized with NH3



Piotential exam questions:

Which feedstock is the most suitable for ethylene production via SC?

A. Ethane
B. Propane
C. LPG
D. PB mix
E. Virgin naphtha
F. Gasoil

- Typical furnace parameters of SC?

A
T= 1000°C
P= 0,3 bar
t= 10 sec
Steam = 0,5 kg/kg

B
T= 650°C
P= 10 bar
t= < 1 sec
Steam = 5 kg/kg

C
T= 830°C
P= 2 bar
t= < 1 sec
Steam = 0,5 kg/kg

D
T= 830°C
P= 200 bar
t= < 1 min
Steam = 0,1 kg/kg

E
T= 830°C
P= 2 bar
t= 1 min
Steam = 10 kg/kg

Plastic industry

2022 429Mta / MOL Group ~1,3MTa

- PE ~117Mta Film & Sheet >> Injection molding > Blow molding > Pipe & Profile
  - HDPE/MDPE 51Mta
  - LLDPE 40Mta
  - LDPE 26Mta

  } Classified by density
- PP >76MTa Injection molding > Film & Sheet > Raffia > Fiber >> Pipe & extrusion >> Blow molding
  - HOMO
  - RACO
  - HECO

  } Classified by stucture

- Good chemical resistance, low S.G., easy to shape
- Reduces overall carbon footprint, cost effective but public image is destroyed by irresponsible waste management.
- High oil price motivates recycling efforts, we may live to see the end of oil era, economic slowdows delays the date.

Some definitions

- Catalyst => Provides active centers during polymerisation on which monomers/comonomers take part in chain growth, can not be recovered, sold with the product

- Monomer => Main building blocks of polymers, e.g.: ethylene propylene butene-1 styrene

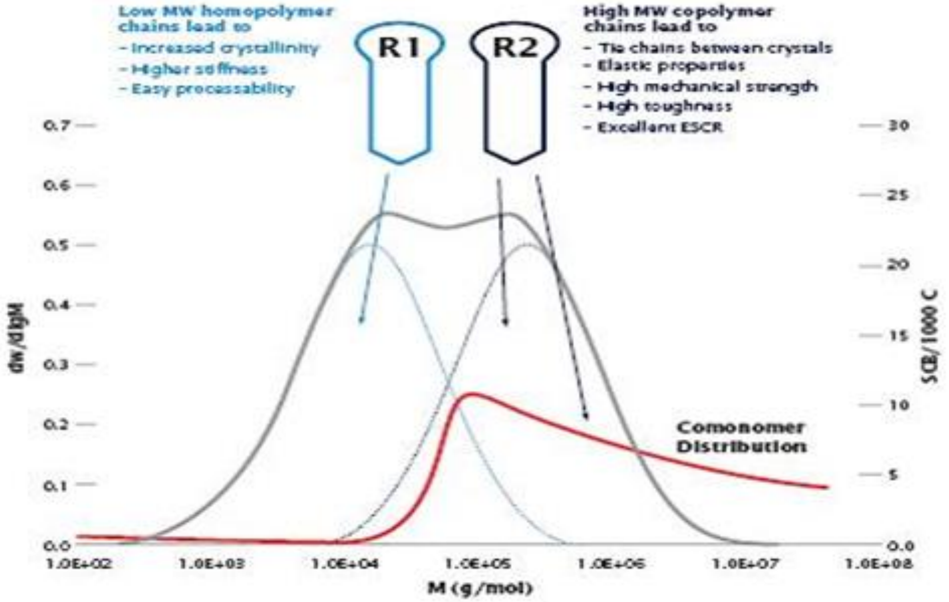
- Comonomer => Secondary building blocks of polymers, modificators e.g.:ethylene propylene butene-1 styrene

- Copolymer => Polymerisation product of a monomer and comonomer

- Oligomer => low molecular weight (100-1000monomer units) usually unwanted side products of polymerisation reactions

- Additives => to improve a specific property, e.g. in case of PP:
  - Fillers=Mica, Talc, $CaCO_3$
  - Reinforing additives=Glass fiber
  - Antioxidants
  - UV stabilizers=HALS
  - Flame retardants
  - Antistatic agents
  - Nucleating angents
  - Other plastics like EPDM to make TPO

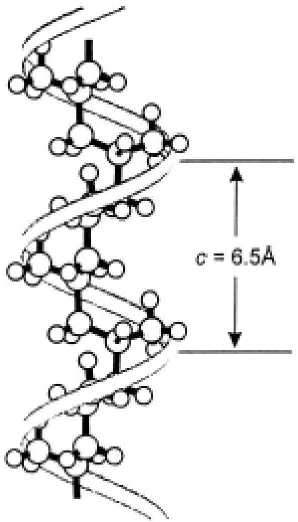
- MW, MWD => Molecular Weight Distribution
  - Multi reactor design=Bimodal capability
  - Single reactor design=Bimodality can only be reached by special catalyst system



Common HDPE types

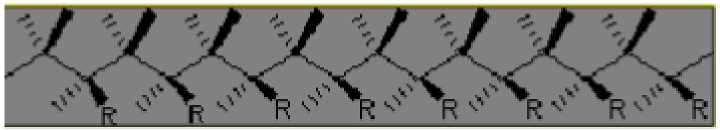
Property	LDPE/MOL	LLDPE	MDPE	HDPE/MOL
Density , g/cm³	0.915-0.935	0.910-0.935	0.935-0.945	0.945-0.970
Melting point (Tm), °C	105-115	115-125	125-130	130-135
MFR (2.16kg/190°C), g/10min	0.2-200	0.3-50	0.05-10	0.05-100
Molecular Weight Distribution (MWD)	Medium/Broad	Narrow, Bimodal	Narrow, Bimodal	Narrow, Broad, Bimodal
Molecular structure				
Chain branching	Both, long & short branches	Many short branches	Some short branches	(Very) few short branches
Copolymers & similars PE´s	EVA, EMA, EEA, EBA, EAA, EMAA	VLDPE, ULDPE		HMWPE, UHMWPE
	High pressure	**Low pressure polymerisation**		

Common PP types & cristallinity



Right-handed Threefold Helix of Isotactic Polypropylene

Isotactic homopolymer



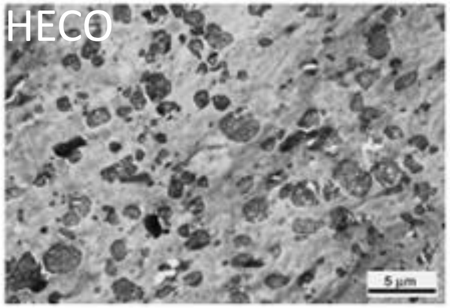
All methyl groups are located on the same side – crystalline

Atactic homopolymer

Methyl groups can be found randomly on both sides – amorph

Syndiotactic homopolymer

Methyl groups location is alternating from side to side – crystalline but not so mutch as Iso.



Homopolimer
HOMO

PPPPPPPPPPPPPPPPPPPPP

Polymer chain is made of propylene only

Random copolimer
RACO

PPPEPPEPEPPPPEPPPEPPP

Polymer chain contains 3-5% randomly incorporated ethylene

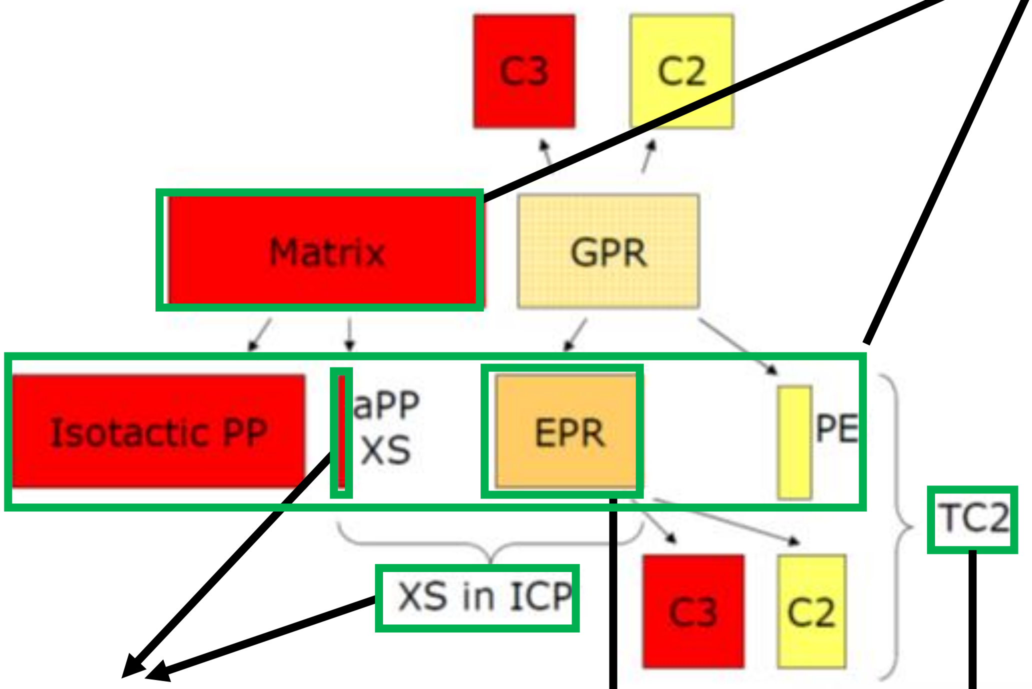
High Impact or Heterophasic copolymer
HECO

PPPPPEEEEEPPPPPEEEEPPP
PPPPPPPPPPPPPPPPPPPPPP

Polymer chain1 is made of pure propylene chain2 is made of ethylene and propylene where ethylene content is 10-30%

HECO PP structure

Measured



Melt flow measurement (MFI or MFR):

Polymer melt throughput in grams at 1,05 mm dia / 8mm length capillary during 10min under different weights* / temps**

*Weight: 2,16 kg – 5,00kg – 21,60 kg
**Temperature: 190°C vagy 230°C
Standard: ISO 1133
Unit: ….g/10 perc [190°C/2,16]

1968-2020 2021-

Cold xylene solubles (CXS or XS) Melt flow measurement [wt%]:

NMR, HPLC, Classic evaporation method

Ethylene content [wt%]

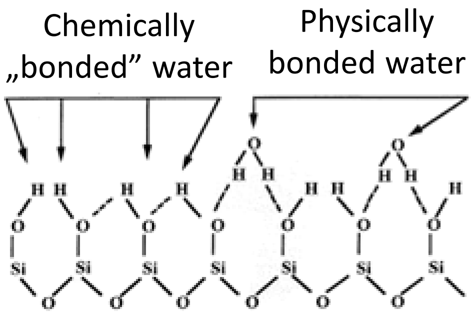
FTIR

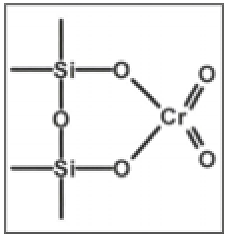
IV of bipolimer [dL/g]

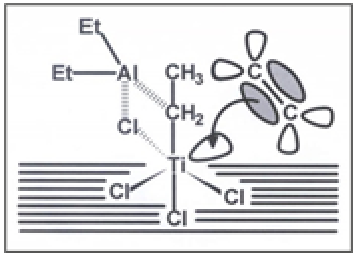
Viscosity meter

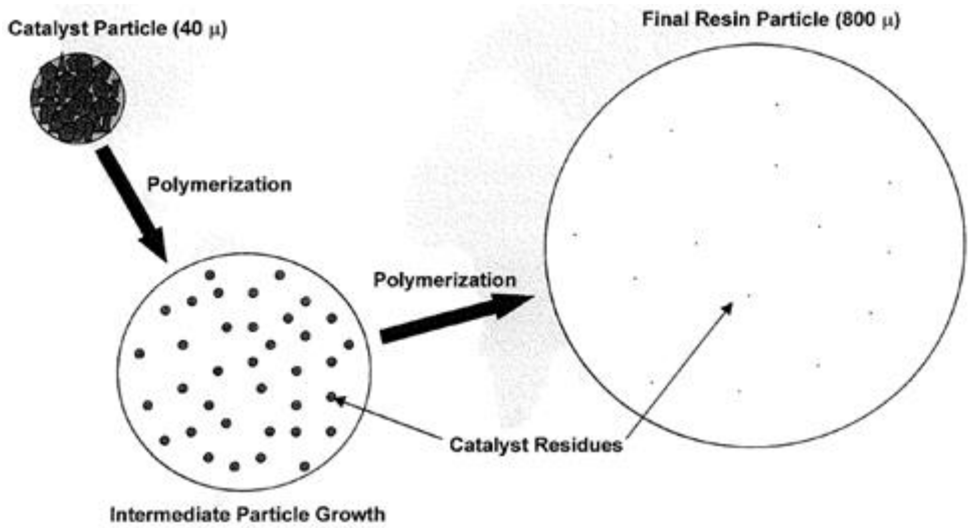
Catalyst systems

- Chromium catalyst for HDPE1
  - Silica supported CrVI
  - Activation is necessary before use
  - Cocatalyst is not necessary
  - For Medium and broad MWD grades
- Ziegler-Natta (ZN) for PP3 PP4 HDPE2
  - $MgCl_2$ supported $TiCl_4$
  - Metal alkyl cocatalyst is needed (TEAL)
  - Narrow or broad MWD
  - Bimodal grades are possible with special catalyst or multi reactor setup
- (Oxygen for LDPE2)
  - It is rather an initiator than catalyst
  - Supressed mini explosions in the reactor generate free radicals which kick start ethylene polymerisation
  - With organic peroxides some final product properties can be controlled



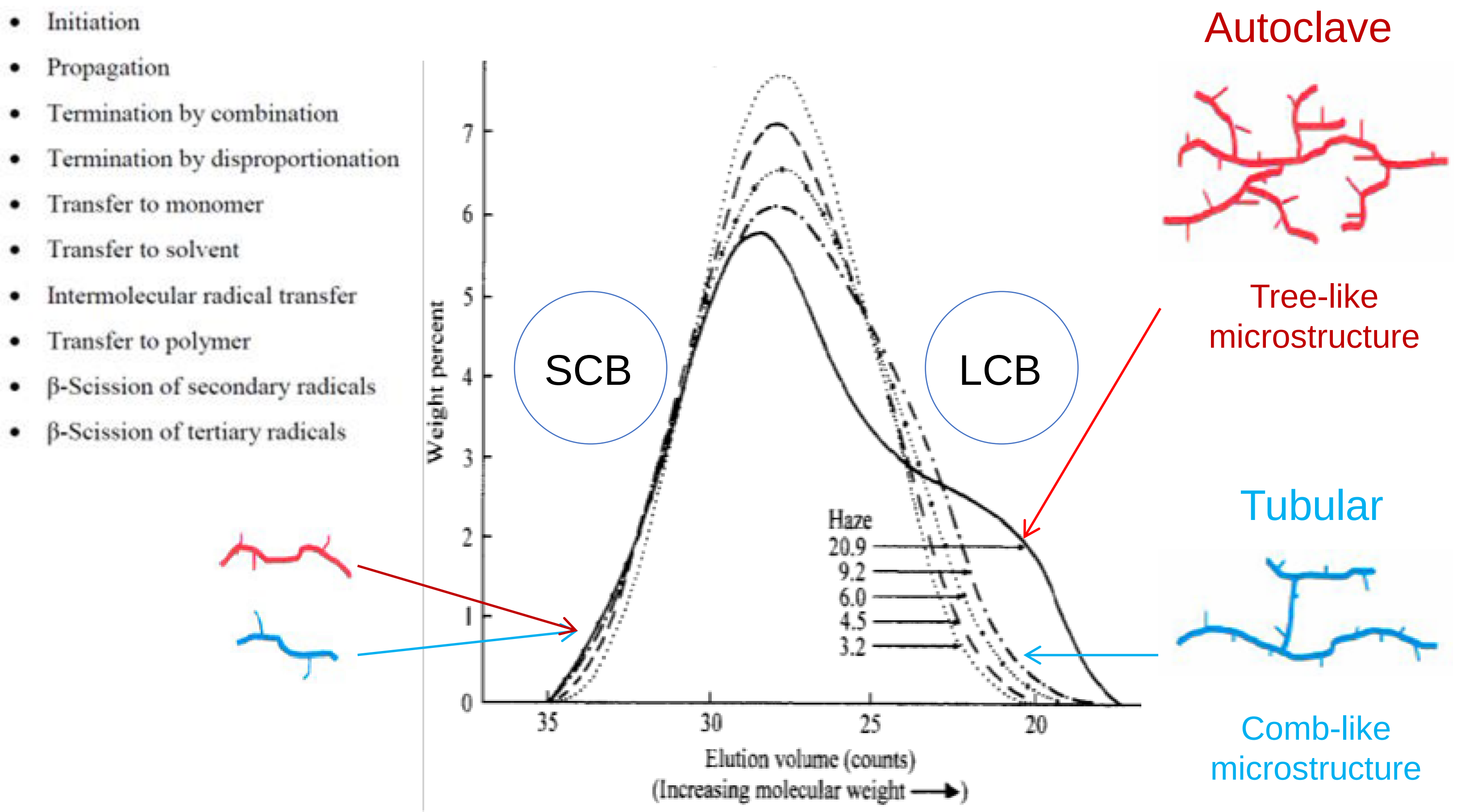






LDPE TECHNOLOGY TUBULAR VS AUTOCLAVE

- Different process conditions lead to product with different properties mainly in terms of MWD and Long chain branches (LCB)



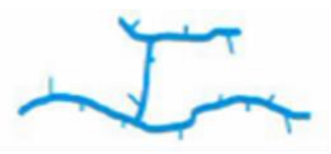
LDPE TECHNOLOGY - TUBULAR VS AUTOCLAVE

Tank reactor

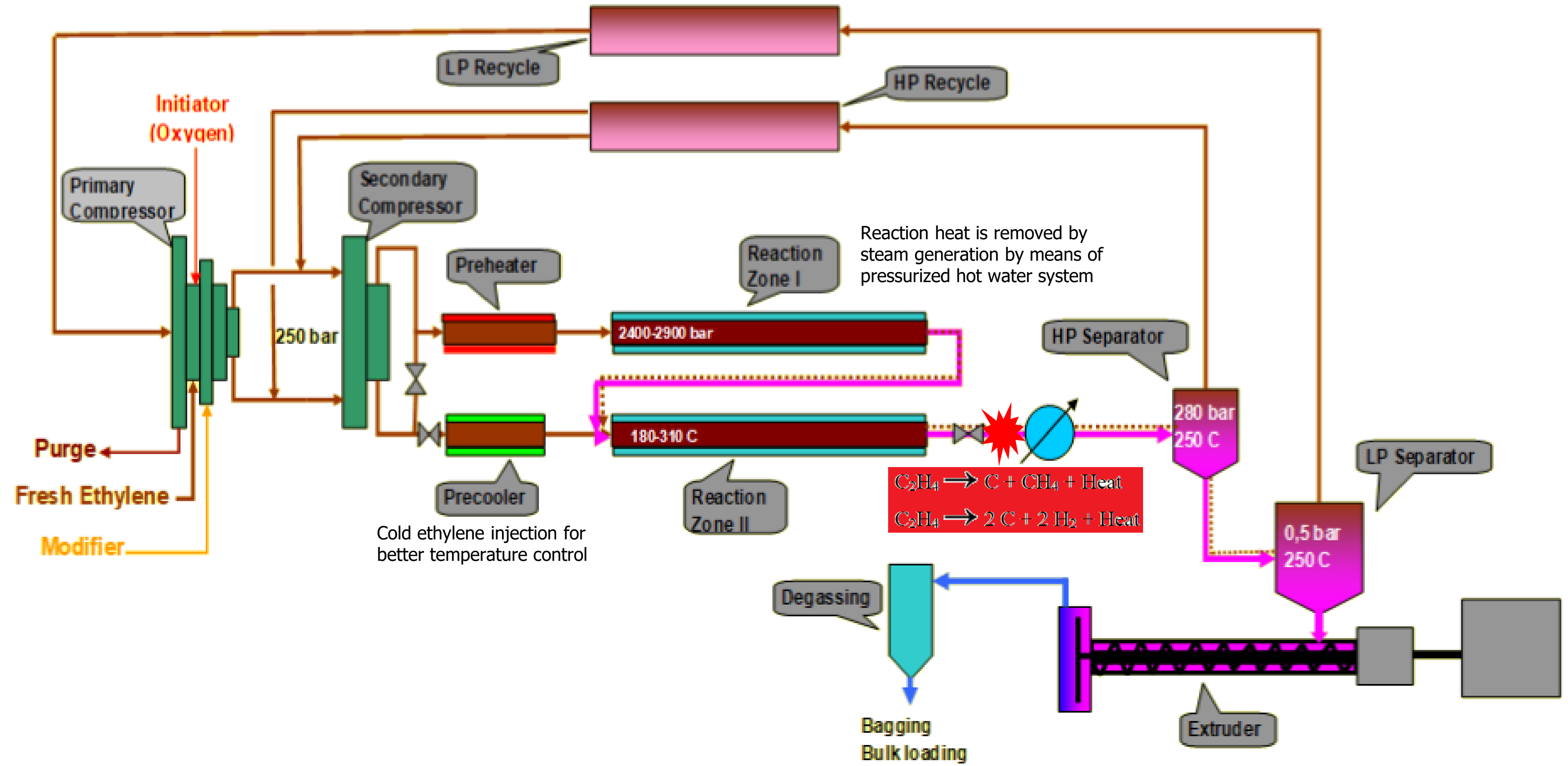
- Conversion ~ 20%
- Polymerisation heat is removed by reactants
- Temp.: 150°C
- Pressure:1300-2000bar
- High capacity hyper compressor is necessary
- Initiator: organic peroxide
- Higher copolymer load is possible 40% LD/EVA
- Small reactor space yield, smaller namepalte capacity, max 150 kta
- Broad MWD

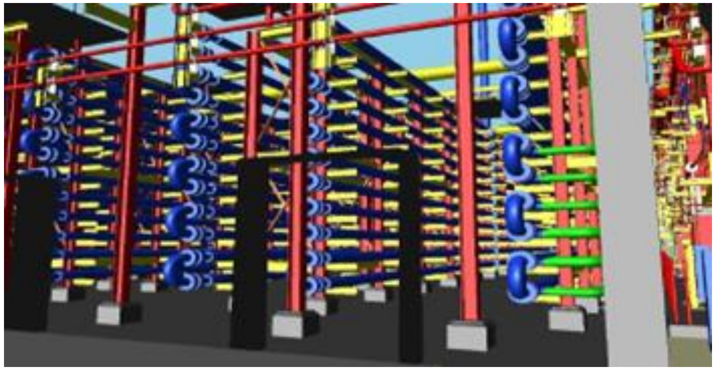
Tubular reactor

- Conversion ~ 40%
- Polymerisation heat is removed by cooling water
- Temp.: 300 - 350°C
- Pressure:2500-3200bar
- Lower capacity hyper compressor for the same capacity
- Initiator: oxygen
- More translarent film, LD/EVA up to 10%
- Bigger throughput, 400 kta
- Narrow MWD



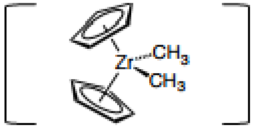
LDPE2 – Technology



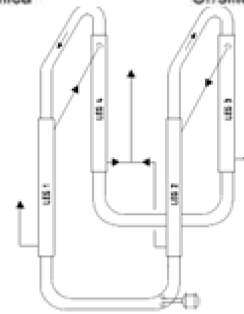


At reaction pressure and temperature LDPE is dissolved in ethylene gas, decreasing the pressure by means of kick-valve will break the homogenity, expansion increases the temperature of the mixture, cooling is needed to avoid polymer degradation and decomposition of ethylene

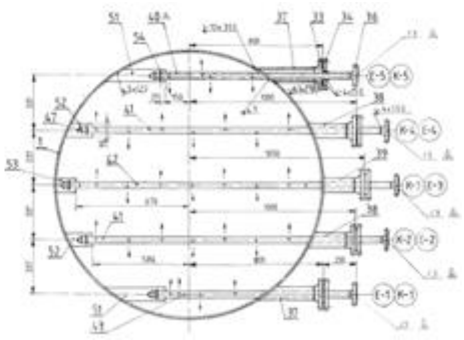
Particle form, loop HDPE1 techn. – Chevron Philips



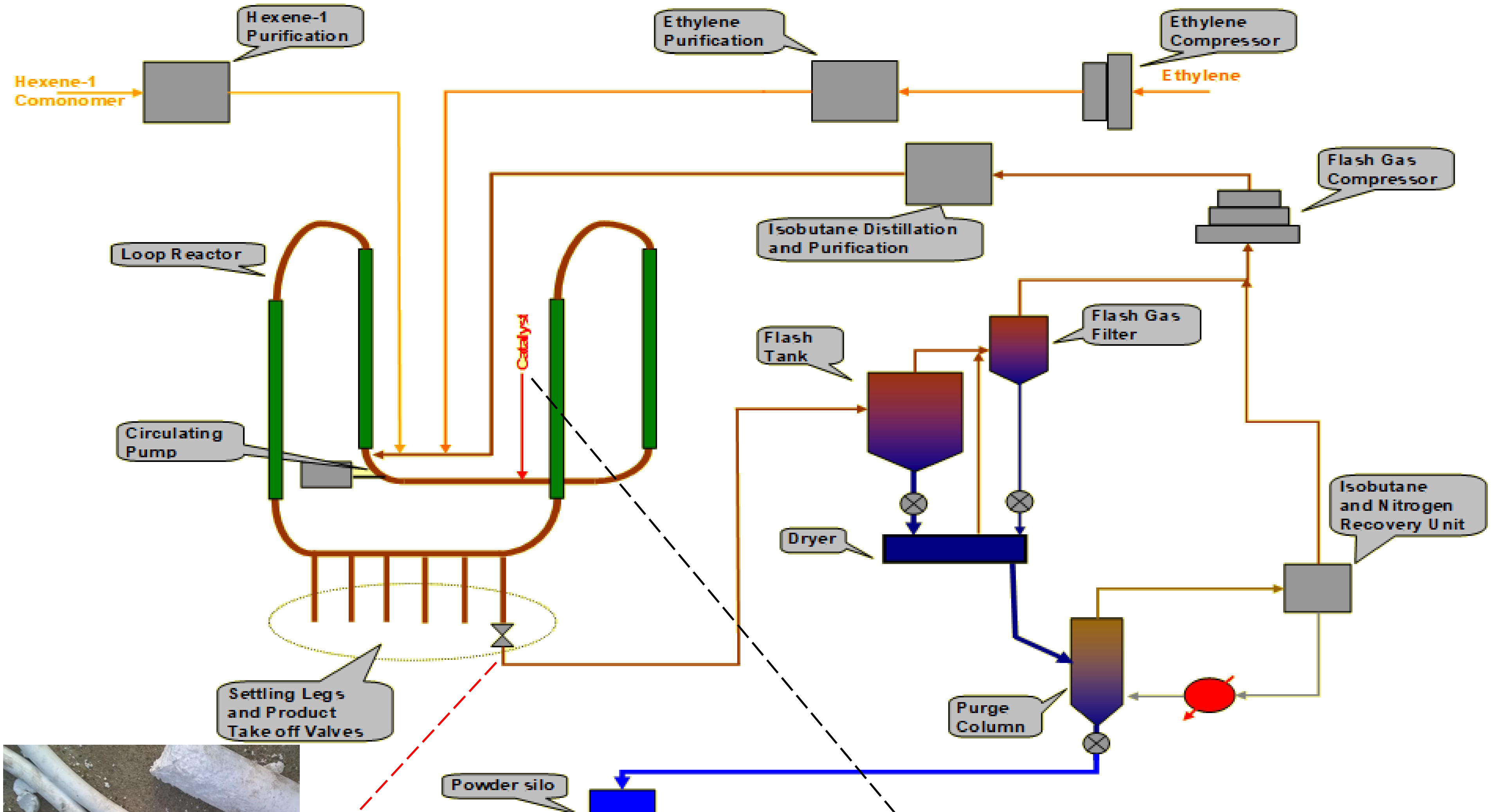

Cr/silica Cr/silica-titania



- Catalyst: Cr, ZN, (metallocene)
- Activation of CrIII to CrVI
  - Fluidized bed activating reactor
  - Oxidation of CrIII by means of hot air 680-790°C / 12-24h
- Reaction conditions in the loop
  - 89-106°C; 42bar
  - 3-6 % ethylene concentration
  - Isobutane as slurry forming agent
  - Polymerisation heat is removed by jacketed reactor section– stable temp. control
  - Hexene-1 comonomer for density control
  - Hydrogen and reactor temperature for chain length control
- Flashing
  - 0,2barg; 50-80 °C
- Degassing
  - 0,1barg; 85°C



HDPE1 – Polymerisation

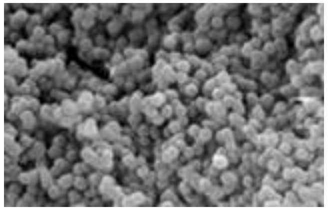


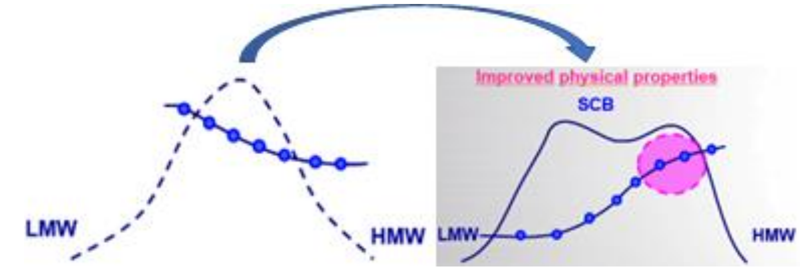
High ethylene, hydrogen, hexene-1, slurry concentration or no flow zones better be avoided

Catalyst feeding with ball check valve

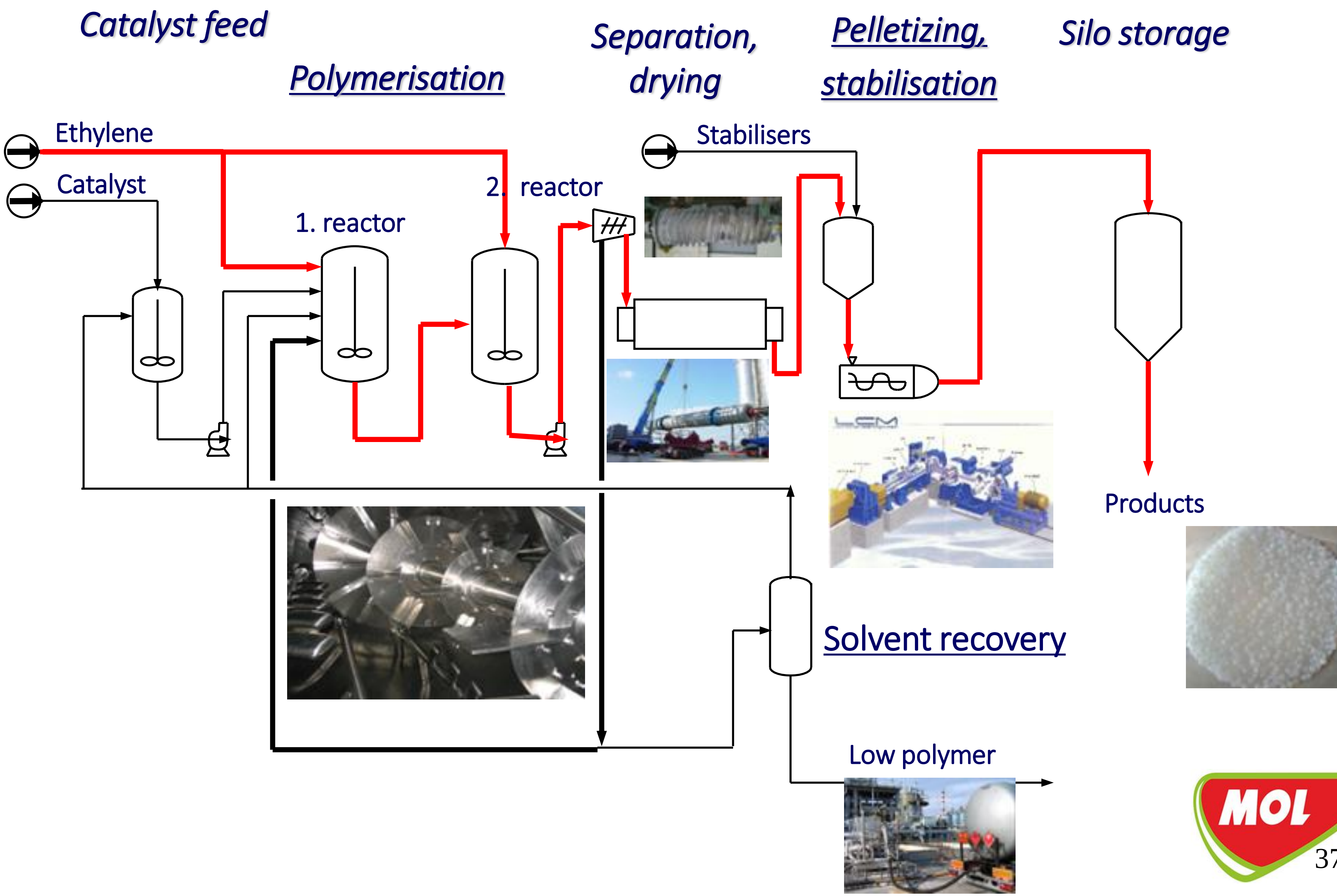
CX Tank reactor, HDPE2 techn. - Mitsui

- Catalyst: ZN 10,000 ～ 30,000 kg-PE/kg-cat
- Low reaction temperature and pressure
  - 6-8 barg, 70-90 °C
- Polymerization heat removal by:
  - Reactor top condensers
  - Slurry coolers
  - Reactor Jacket
- Bimodal grades
  - Different MW production in the reactors
  - Comonomer incoroporation into the longer chains
- Slurry forming hexane and polymer separation with centrifuge
- Hexane purification and low polymer separation
- Comonomer: butene-1, propylene





HDPE2 – Polymerisation & Extrusion

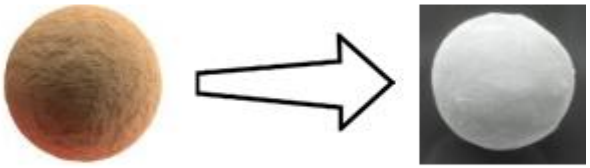


Spheripol Loop reactor PP techn. - LyondellBasell

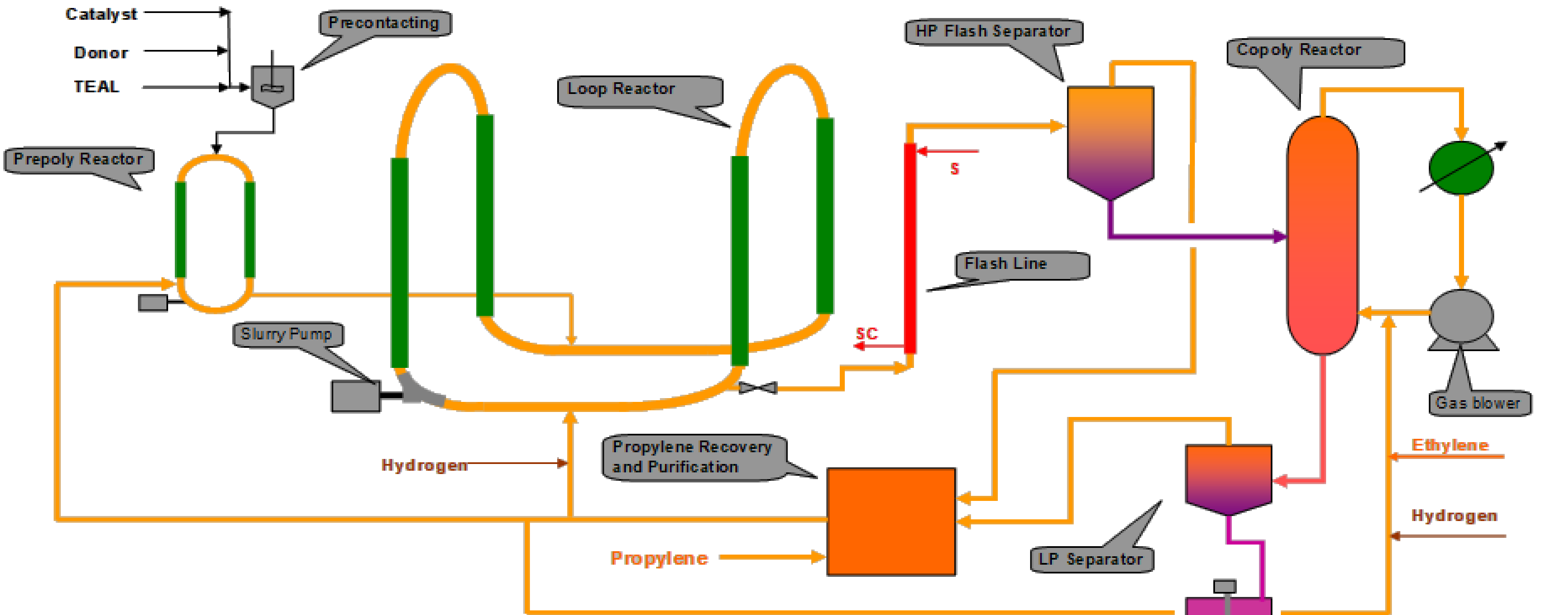
- Catalyst: ZN 30,000 ～ 80,000 kg-PP/kg
  - Various ID and powder morphology types
- Low reaction temperature medium pressure
  - 70°C, 38barg
- Polymerization heat removal by:
  - Jacketed vertical loop reactor sections
- Bimodal grades
  - Different MW production in the reactors
- Bulk polymersiation
  - Slurry forming media is liquid monomer
- Flashing step
  - To recover 85% of monomers
  - 2 step flashing to 18barg (HP) then 0,8barg (LP)
  - Gas phase reactor is operated between HP and LP pressures ~12barg
- Steaming & Drying step
  - To recover 15% monomer
  - Deactivate catalyst system

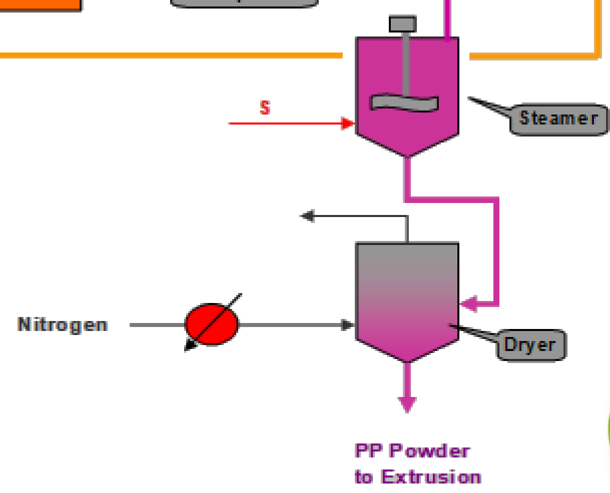
Process step	Temperature °C	Pressure barg
Catalyst activation	10	40
Prepolymerization	20	35-38
Polymerization - loop reactors	70	34
High pressure separation	90	18
Polymerization - gas phase reactor	75-80	10-14
Steaming	105	0,2
Drying	90	0,1

One catalyst grain will make one PP sphere



PP3 PP4 – Polymerisation



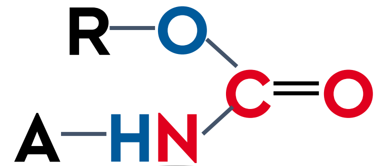


Polyols

APPLICAITONS

R-OH

$O=C=N-A$



POLIOLS + **IZOCYANATES** = **POLYURETHANES (PUR)**

+ additives

Triols with long polyether chain — Flexible


Matress


Car seat


Furniture

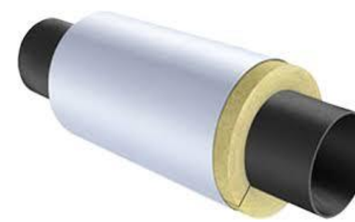

Car interior

Sugar and triol based polyols with short polyether chain — Rigid


Panels


Cold insulation


House insulation


Pipe Insulation

Diols with various polyether chain length — Non foam

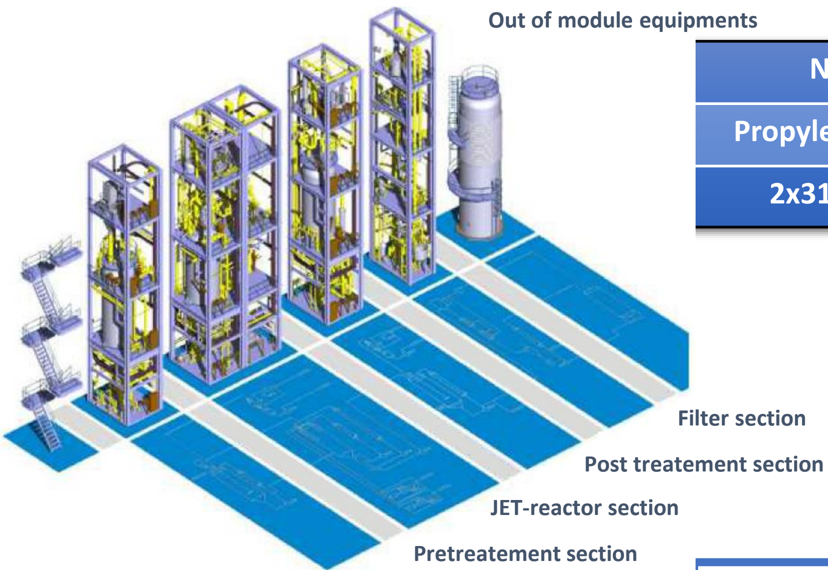

Paint


Adhesive


Sealant

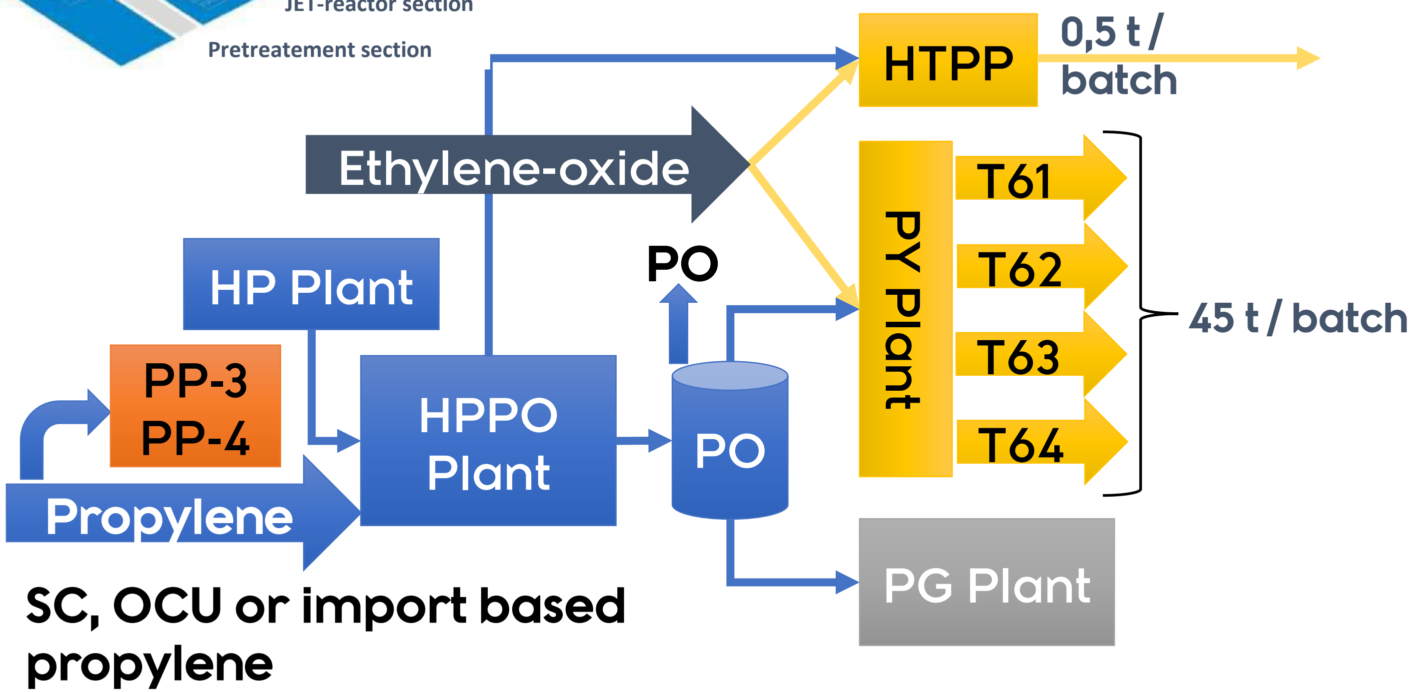

Elastomer

POLYOL COMPLEX FOR OLIGO POLYETHER POLYOLS

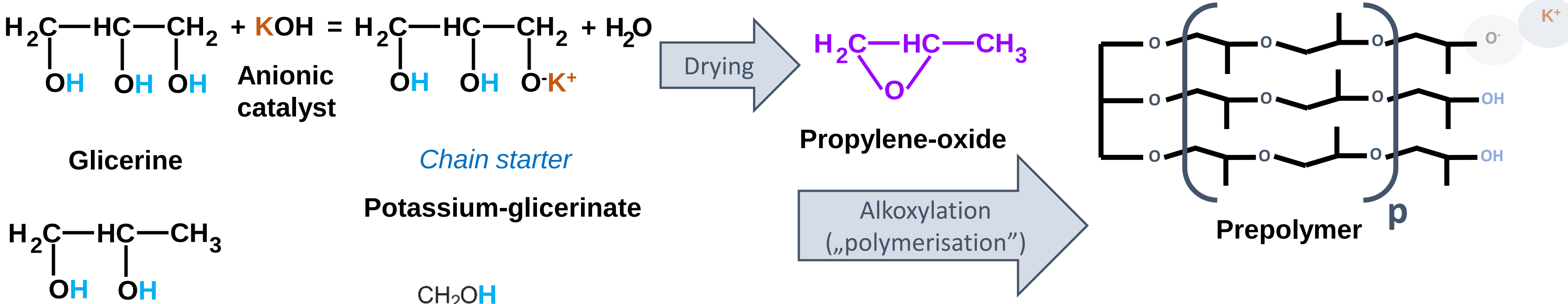


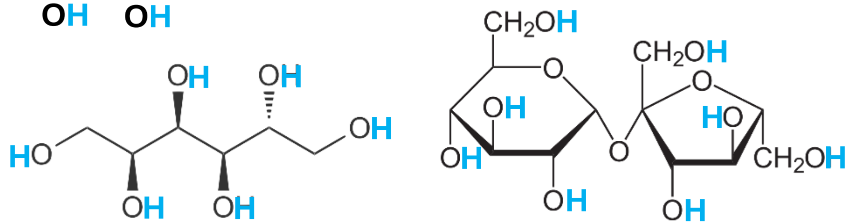
Nameplate storage capacity	
Propylene-oxide	Ethylene-oxide
2x3182 m3	2x500 m3

Plant	Namplate capacity on product
HP	138 kta
HPPO	200 kta
PO	20 kta
PY	205 kta
PG	60 kta



Reactions

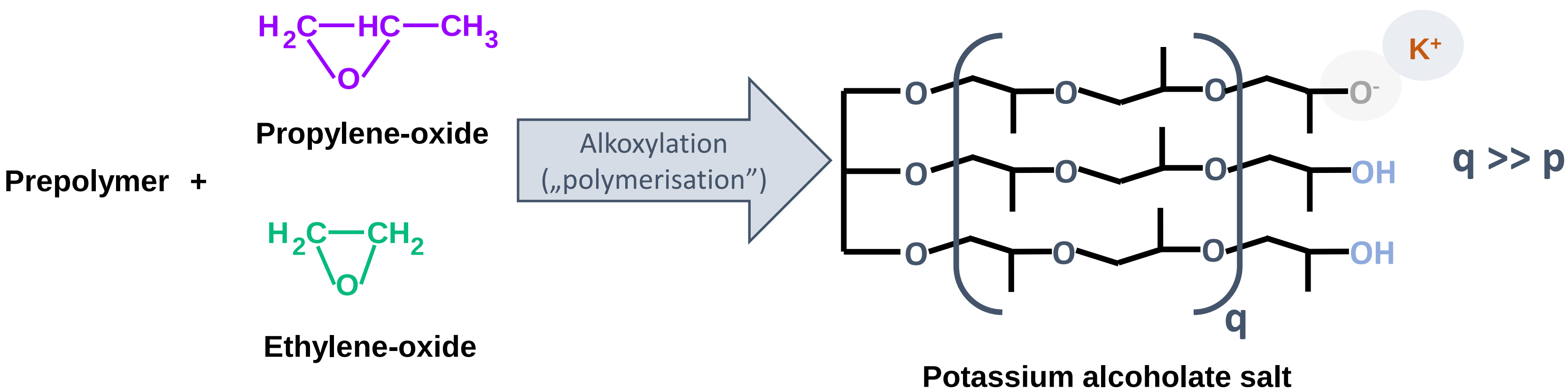




Prepoly reactor

- Alkoxylation in batch mode, Pressure from 80mbara-2barg to 9-13barg @ 120°C
- 50,0 m/m% KOH: 270 - 600kg for 45ton of Polyol

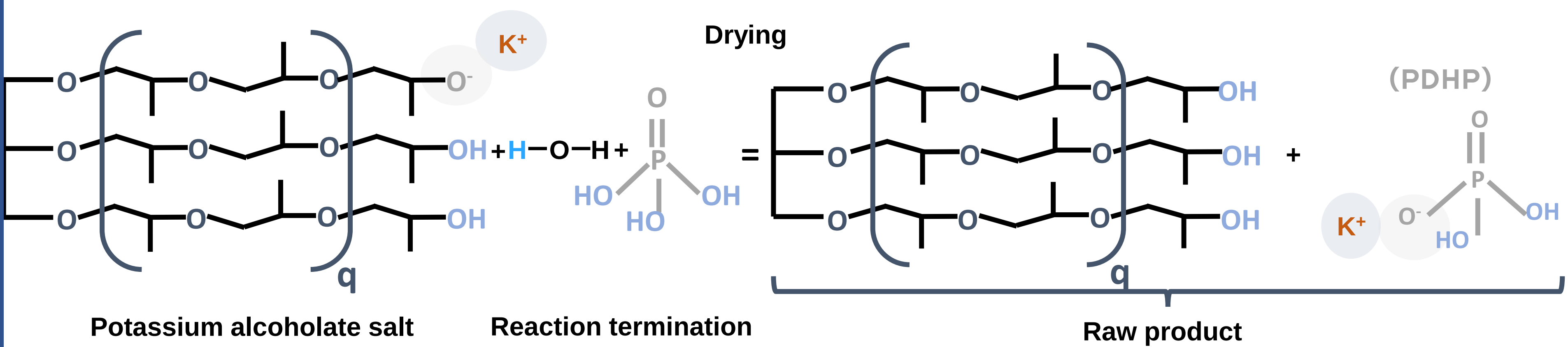
Jet reactor



- Pressure trends are followed by DCS to avoid EO decomposition

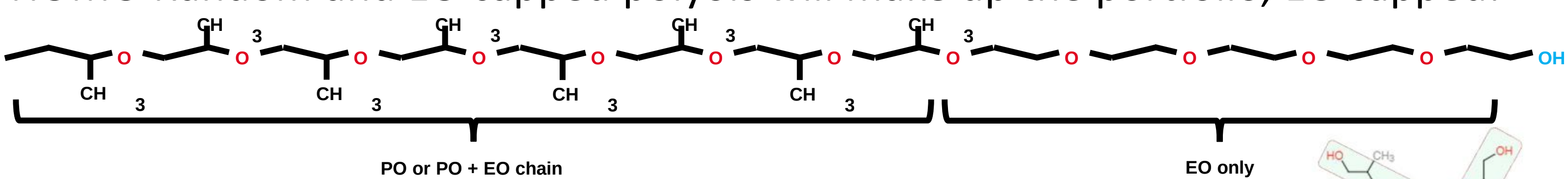
Reactions

Post treatement

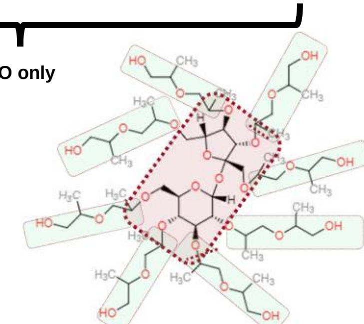


- Raw product → Filtering → Mixing → Stabilisation → Final product

- 45ton/batch, main parameters=MW, hydroxyl number, viscosity
- Starter mole number & used oxides and their amount define the product
- Functionality of starter mix define the functionality of product
- Low MW=100-1000g/mol Medium MW=1000-3000g/mol High MW >3000g/mol
- HOMO Random and EO capped polyols will make up the portfolio, EO capped:



- Sucrose based HOMO polyether polyol with 1150g/mol MW
- Product is relatively harmless pale yellow or white liquid



Thanks for your attention!