Maleic anhydride (MAn) production

Tamás Németh
Technology Development

tamnemeth@mol.hu

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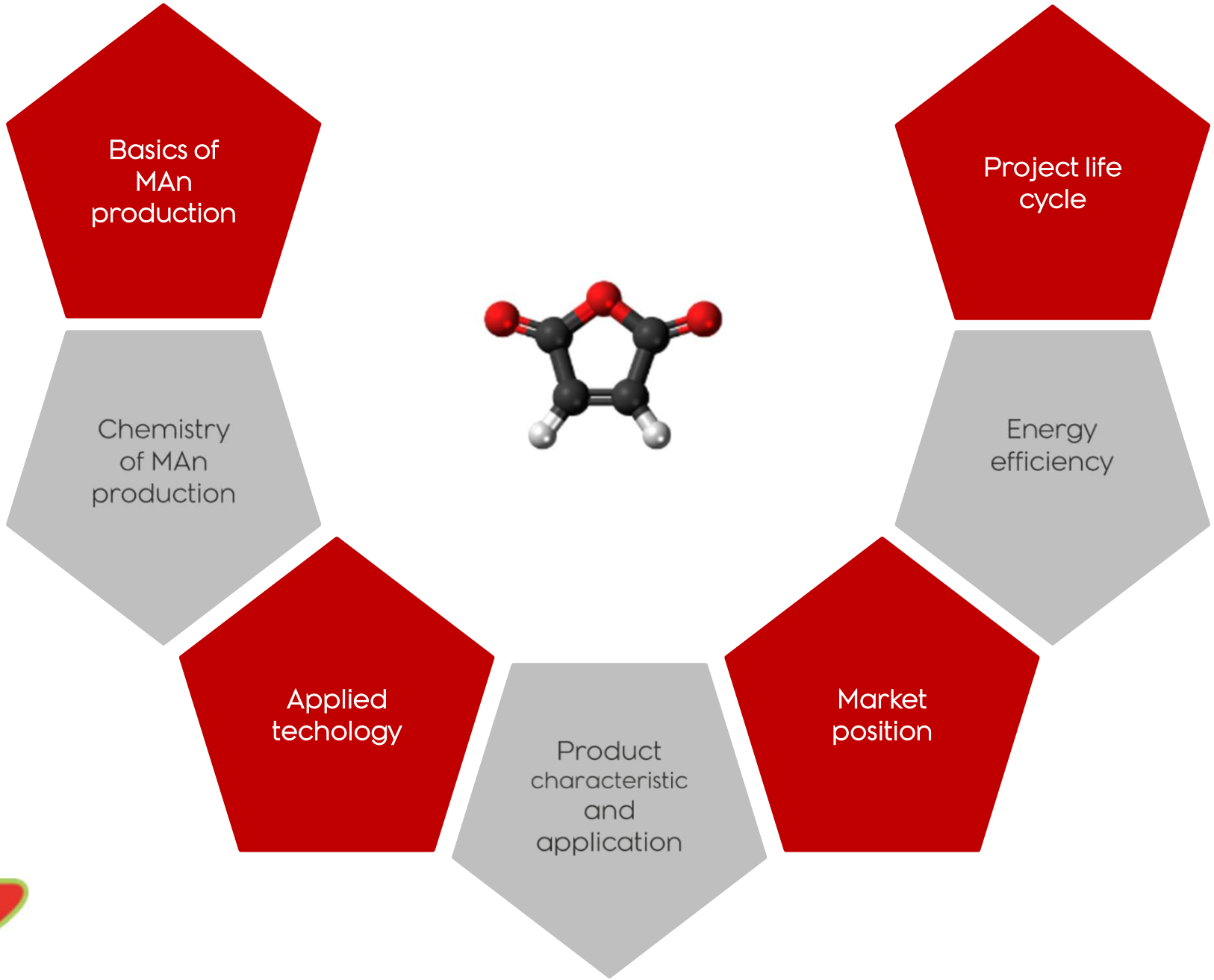
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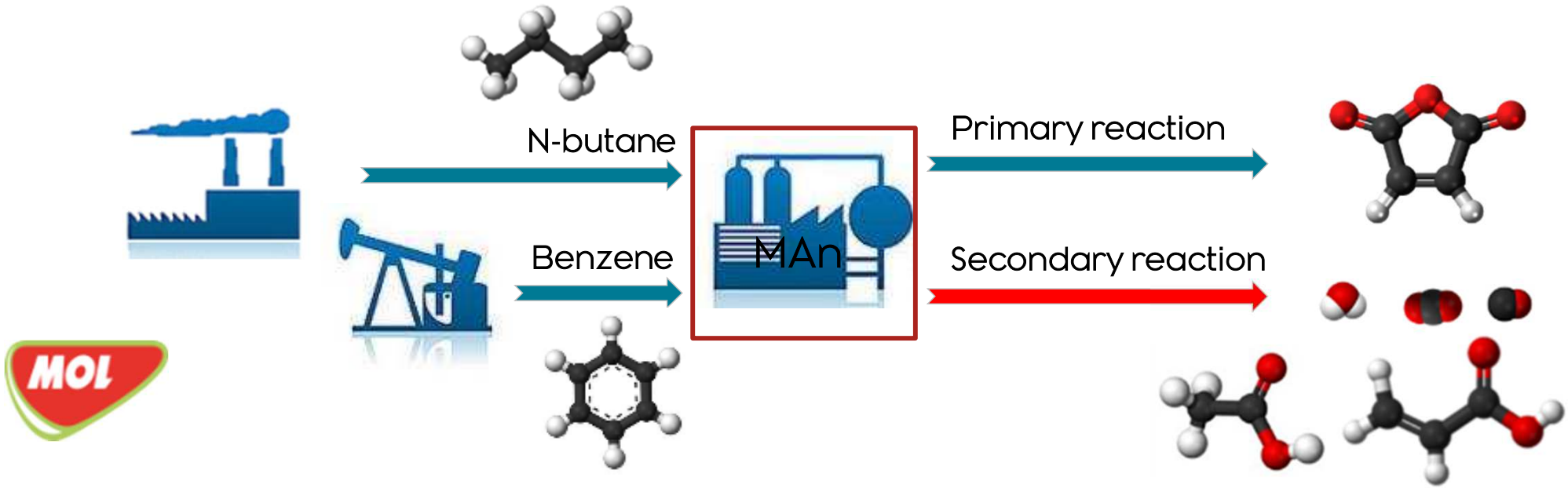
Maleic anhydride production

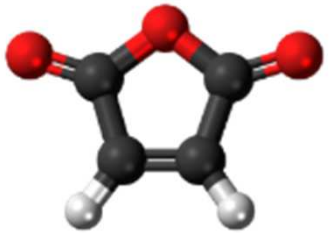
Basics

- MAn production is typically a petrochemical process. It is not part of the traditional refinery structure.
- The MAn has normally been produced by two ways: the partial oxidation of n-Butane or Benzene by the addition of air in the presence of a catalyst.
- The Dunai Refinery has sufficient quantities and quality of n-Butane (nC_4) feedstock for MAn production, as the nC_4 used as feedstock is sourced from the Gas Fractionation Plant (no market exposure).
- During the MAn production reaction:
  - as primary reaction Maleic acid and water...
  - ...as a secondary reaction, carbon dioxide, carbon monoxide, acetic acid and acrylic acid are also produced.
- Hydrocarbons apart from nC_4 in the feedstock trigger the secondary reactions.

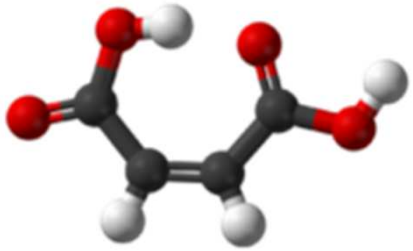


Maleic anhydride production

Basics

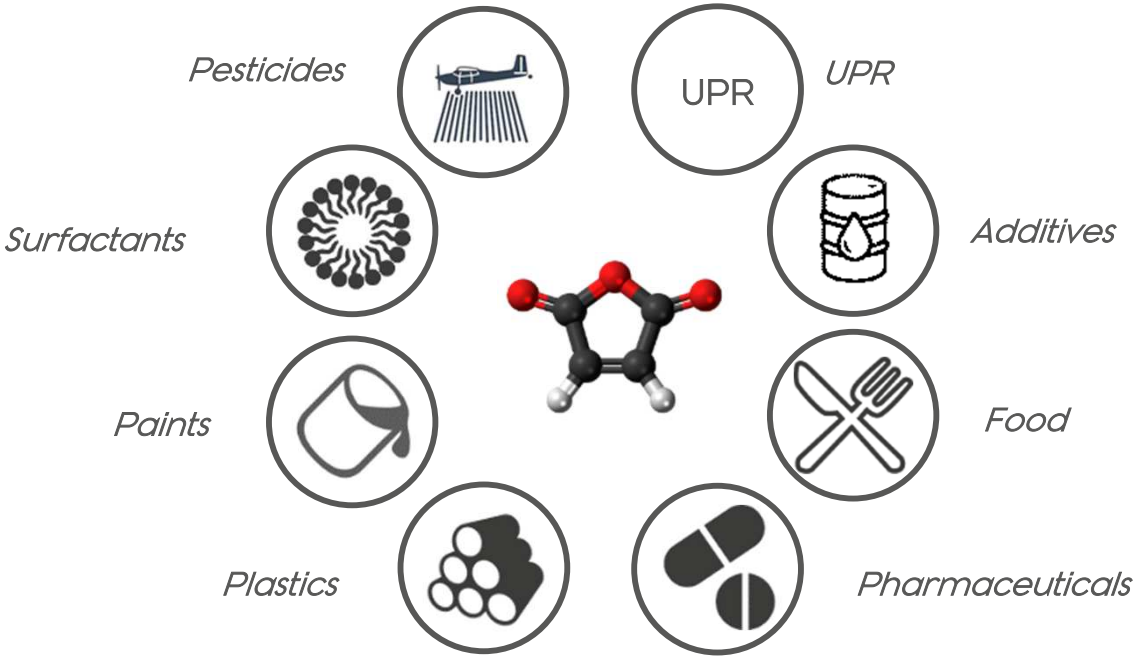


Maleic acid Anhydride (MAn)



Maleic acid (MA)

- MAn is a white crystalline substance at room temperature. Very hygroscopic and dissolves well in water.
- It is commercially available in liquid and pastille form.
- Due to its chemical nature, it is suitable for both polycondensation and polyaddition reactions and therefore has a wide range of applications.



Maleic anhydride production

Chemical reactions

- MAn production is an exothermic reaction. The amount of heat released depends on the type of reaction.
- When the nC_4 feedstock is not in contact with the catalyst, the heat and oxygen in the system catalyse the combustion.
- The aim is to reduce secondary reactions to reduce yield and increase plant availability..
- Production from benzene requires more O_2 and the primary reaction produces CO_2.

Primary chemical reaction:

$$nC_4H_{10} + 3{,}5O_2 \xrightarrow{400 \div 405°C} C_4H_2O_3 + 4H_2O - 21.400kJ/kg$$

Secondary chemical reactions:

1. $nC_4H_{10} + 4{,}5O_2 \rightarrow 4CO + 5H_2O - 26.270kJ/kg$
2. $nC_4H_{10} + 6{,}5O_2 \rightarrow 4CO_2 + 5H_2O - 45.725kJ/kg$
3. $nC_4H_{10} + 4{,}5O_2 \rightarrow CH_3 - COOH + 2CO_2 + 3H_2O - 31.400kJ/kg$
4. $nC_4H_{10} + 3{,}5O_2 \rightarrow CH_2 = CH - COOH + 3H_2O - 22.760kJ/kg$

The released heat is the half of simple combustion of nC_4 what means significant heat production during MAn production

MAn technology

Introduction of MOL DR MAn unit

- 1976: The MAn plant is launched. Russian technology. The raw material: benzene.
- 1987: Scientific Design revamp. Feedstock replacement from benzene to n-butane.
- 2006: TechnoBell revamp. Installation of new reactor. Decommissioning of the two old Soviet short-tube reactors.
- 2014: TechnoBell revamp. Capacity increase phase 1..
- 2015: Capacity increase phase 2.
- 2017: New MAn plant project preparation, start of design phase.

MAn technology

Major steps

- Oxidation of nC_4 to maleic acid

  The butane is evaporated. The vapor has been superheated and mixed with air in appropriate proportions. The nC_4 / air mixture is passed through tubes filled with a catalyst containing vanadium pyrophosphate embedded in a salt melt. The catalytic oxidation of nC_4 results in the primary chemical reaction: Maleic anhydride.

- Separation of raw MAn

  From the reaction mixture obtained in the exothermic reaction, MAn is separated by cooling and absorption. During cooling, part of the crude MAn is condensed and separated from the reaction gases. After cooling, the remaining MAn in the reaction mixture is recovered by aqueous washing. The aqueous absorption yields a 40-42 % maleic acid (MA) solution.

- Dehydration a distillation of maleic acid solution

  The MA solution obtained during absorption is dehydrated (batch process) by using a xylene mixture. Dehydration is a stepwise operation consisting of the following steps:

  - Dehydration
  - Acrylic acid removal
  - Xylene removal
  - MSA refining

- Packaging and delivery of distilled MAn

  The main mass of refined MAn is delivered from the unit in liquid form, the rest being filled into bags after pelletising

- Destruction of hydrocarbon-containing tail gases and residues

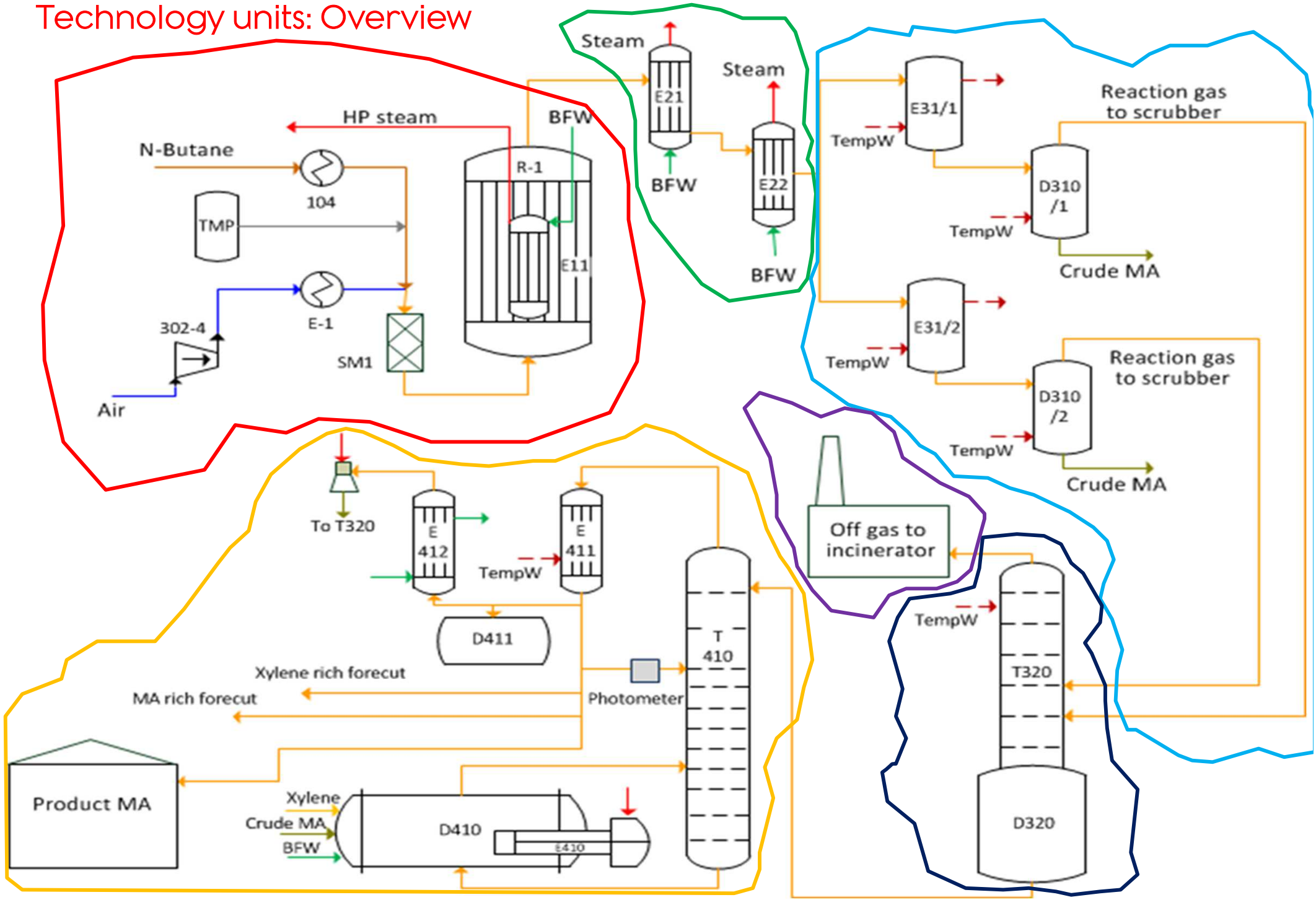
  The residues and CH-containing gases are combusted in the tail gas incineration unit (steam generation).

- Treatment of acid water produced in the process.

  Acidic effluent from the operations is neutralized by NaOH dosing and sent to the biological treatment plant.

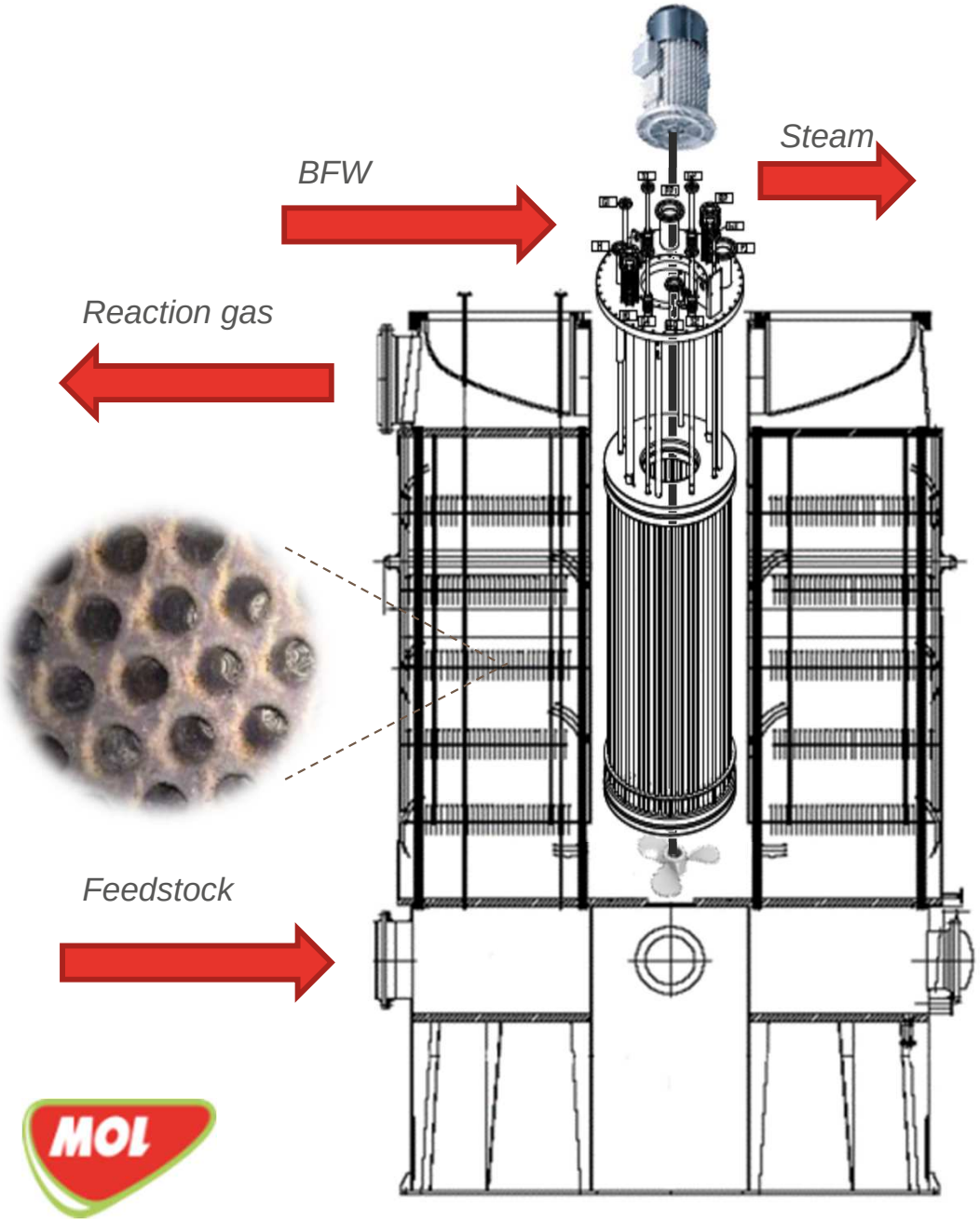
MAn technology

Technology units: Overview



MAn technology

Technology units: Reactor



- The MAn reactor is a shell and tube heat exchanger with more than 20 thousand tubes (ID:21 mm).
- Inside the tubes the catalyst has been loaded in 1-3 layers, depending on supplied type of catalyst.
- Since the reaction forming MAn from nC_4 is strongly exothermic the generated heat is absorbed by molten salt.
- The heat from molten salt has been utilized by another heat exchanger located in the center axis of reactor tubes. The molten salt flows on shell side of both heat exchanger and transfers the heat from molten salt to boiler feed water in tube side of internal heat exchanger and produce high pressure steam (40 barg)
- In order the salt circulation to be sufficient a salt mixer located in the middle of internal heat exchanger.

MAn technology

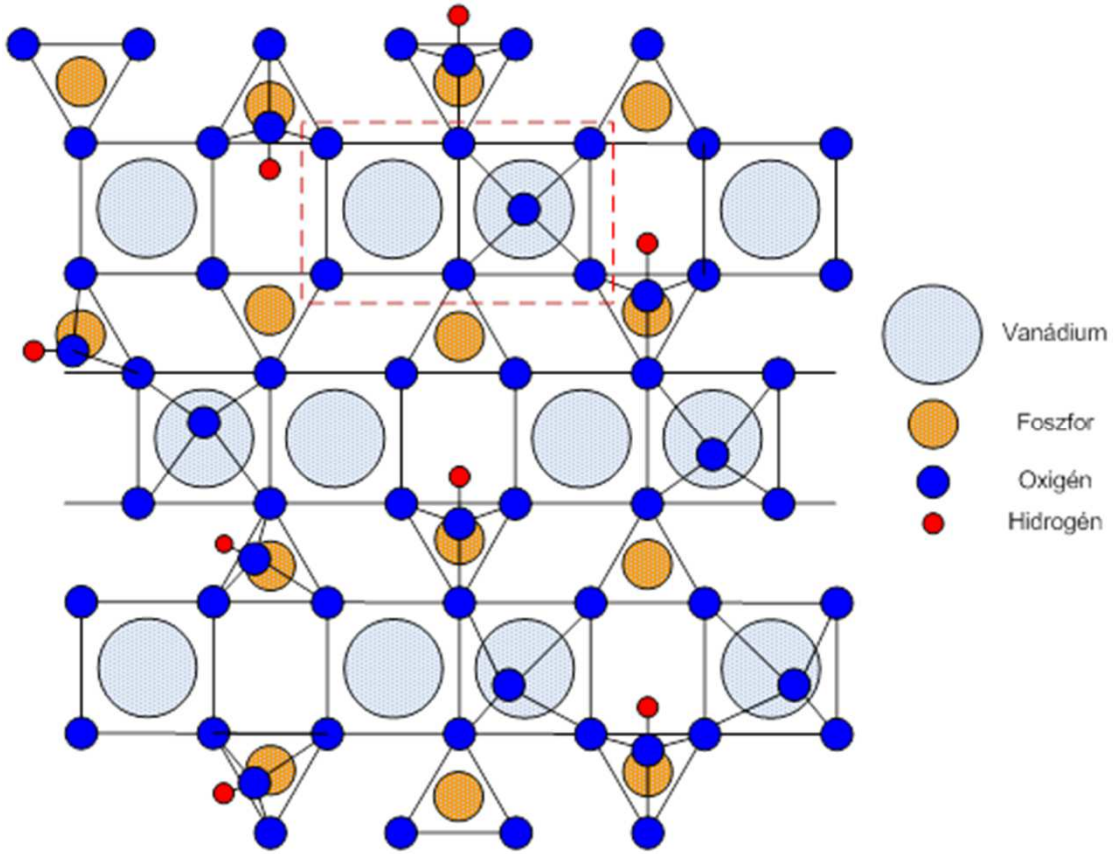
Technology units: Reactor

Operational parameters:

- Inlet nC_4 concentration max: 1,8-2,1 mol%. Pressure: 1,4 barg.
- Inlet nC_4 volume: 72 t/day (~1150 Nm^3/h).
- Inlet air volume: 60-65 th Nm^3/h
- Salt temperature: 420-425 °C. $NaNO_2$, $NaNO_3$, KNO_3 mix. Circulation: 5-6,5 th m^3/h
- Hot-spot max: 520 °C
- TMP dosing for : 0,6 kg/h
- Conversion: min 82%
- Steam production: 12-15 t/h, 360 °C, 38-39,5 barg.
- The feedstock inlet temperature: 130 °C
- Reaction product outlet temperature: 425 °C
- Salt mixer rpm: 550 1/min

MAn technology
Technology units: Catalyst

At high reaction temperature, the equilibrium of the V-O-P bond is disrupted due to the loss of phosphorus. Phosphorus can be replaced by adding TMP (trimethyl phosphate).

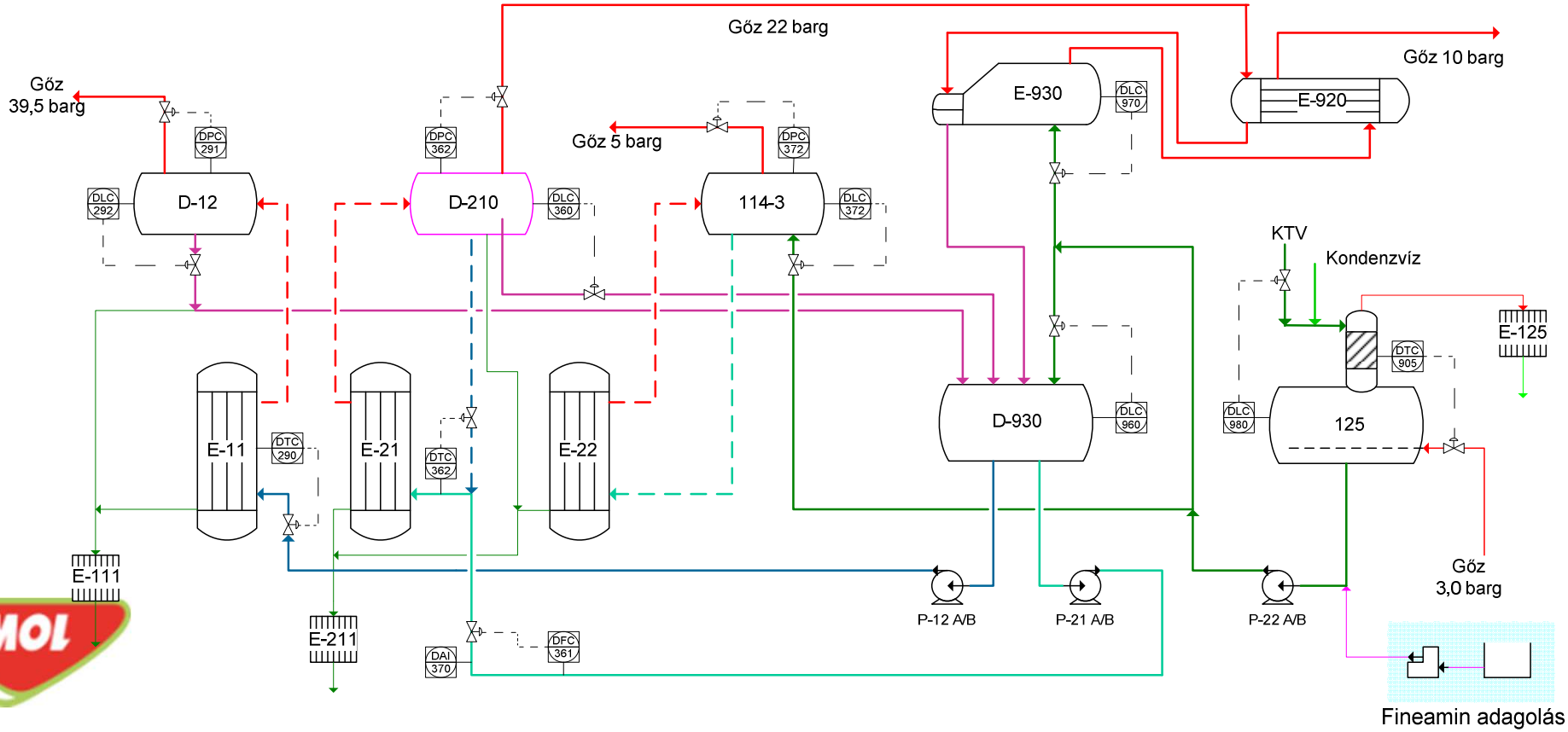


Vanadium pyrophosphate catalyst structure

MAn technology

Technology units: Gas cooler

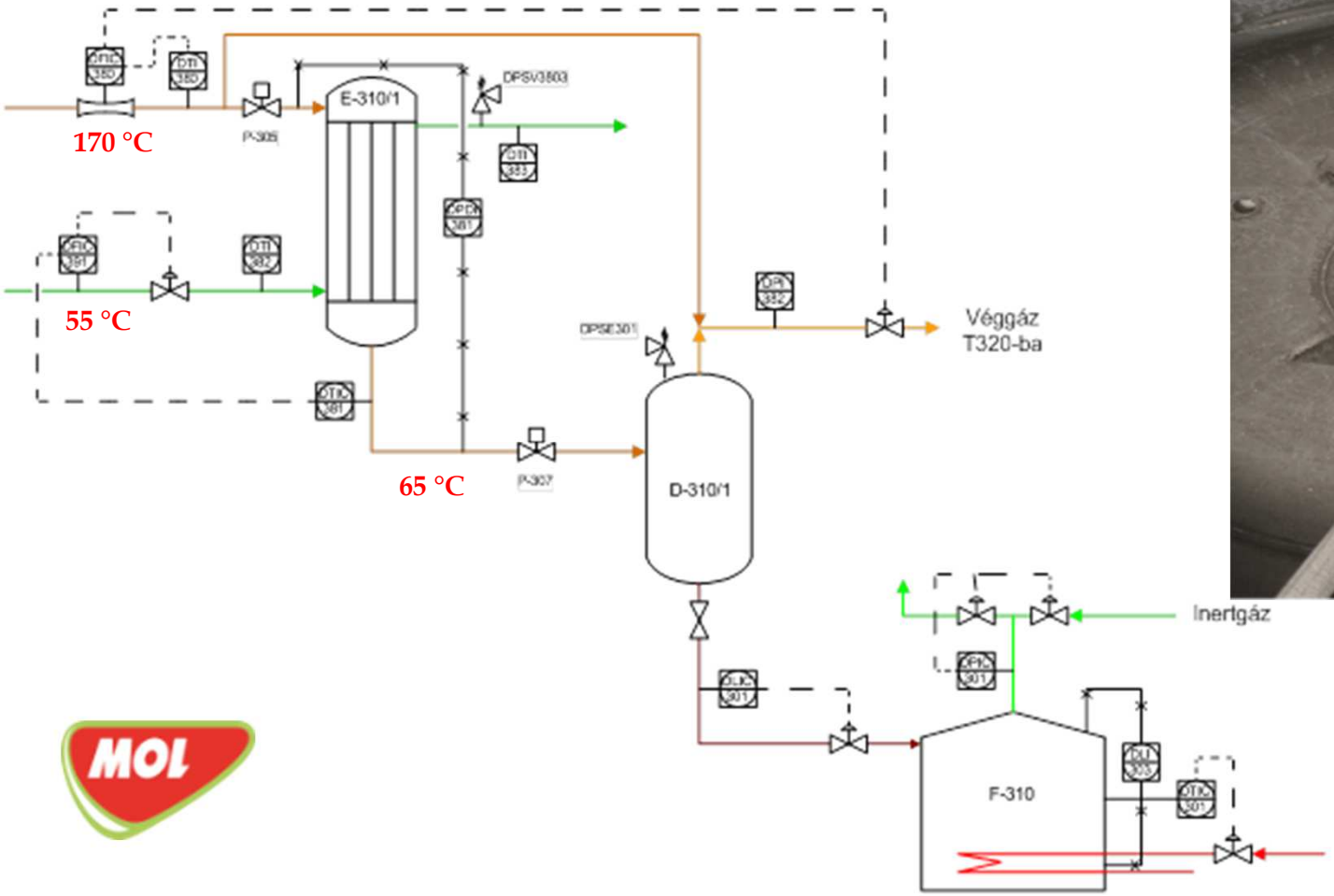
- Downstream unit of MAn reactor. The reaction gas enters the coolers of No. E21 and E22 and exchange the heat with Boiler Feed Water (BFW). The first cooler is able to produce steam at 20-22 barg conditions while the second at 4-6 barg condition.
- The BFW is needed for steam, production has been handled in deaerator No. 125.
- The reaction gases are cooling down to 170°C and entering partial condensers.

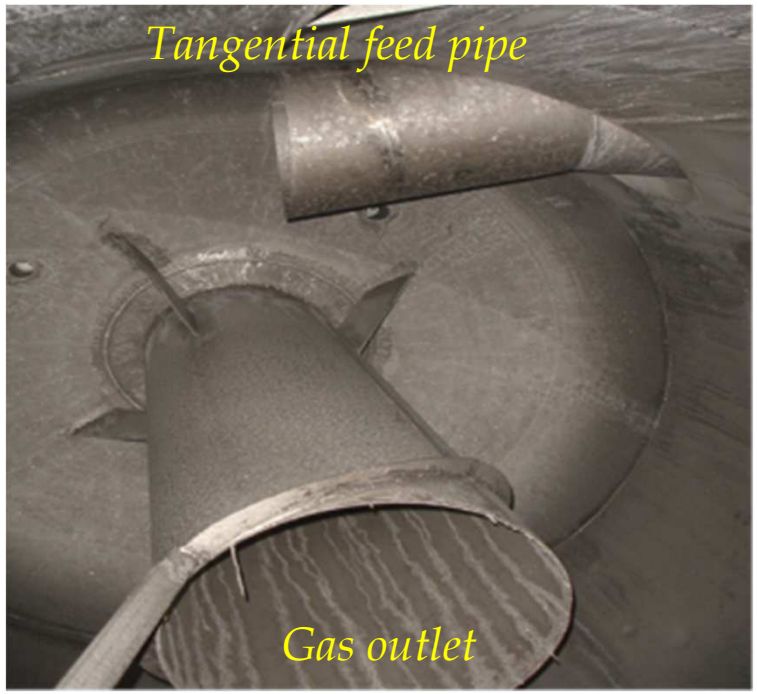


MAn technology

Technology units: Partial condensation system

- Reaction gas enters to condenser and has been cooled down further by tempered water.
- Downstream pipeline of condenser enters to the separator tangentially with decreased diameter what results higher velocity of stream to separator. Due to the centrifugal force the droplets precipitates from gas and has been collected in tank.
- Approximately the 50-55% of the MAn from reaction product has been separated in partial condenser.

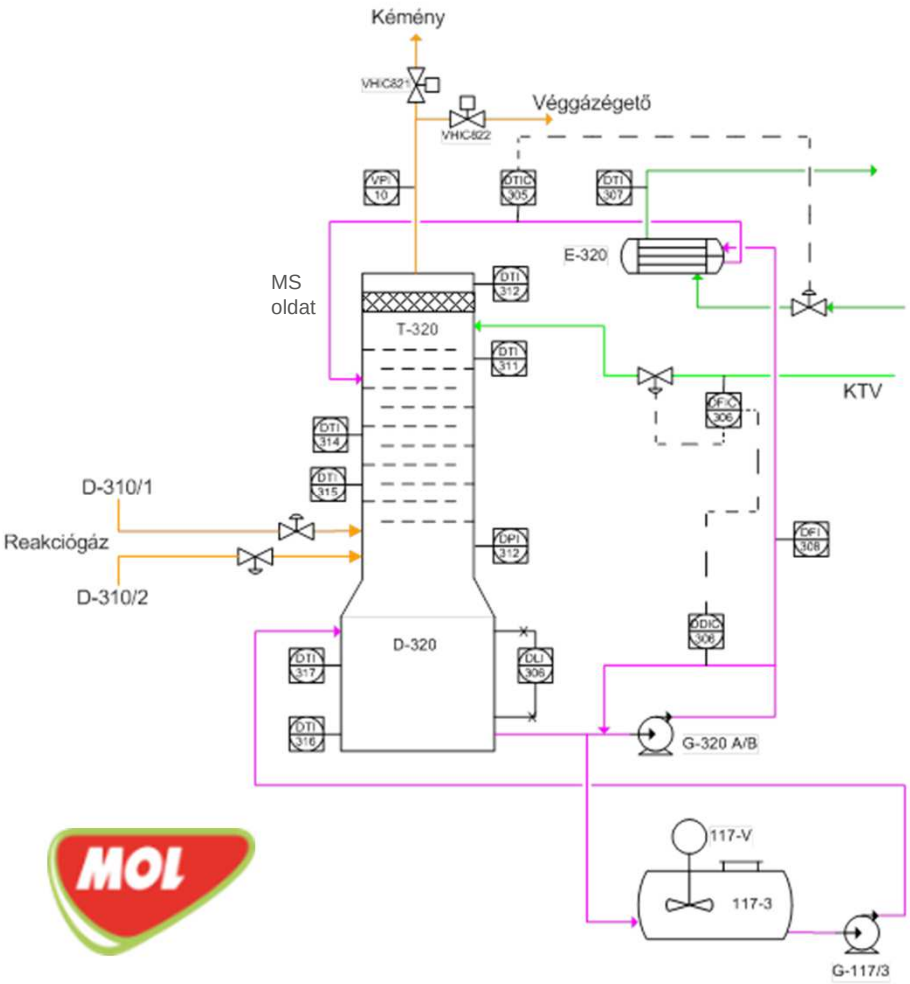




MAn technology

Technology units: Absorption system

- Approximately the 50-55% of the MAn from reaction product has been separated in partial condenser but the rest still exist in reaction gas what has been recovered by absorber (T-320).
- The rest of the MAn from reaction gas is absorbed by MA solvent
- There is water addition on the top of the absorber in order to adjust concentration for the appropriate level and avoid / minimise MA solvent loss

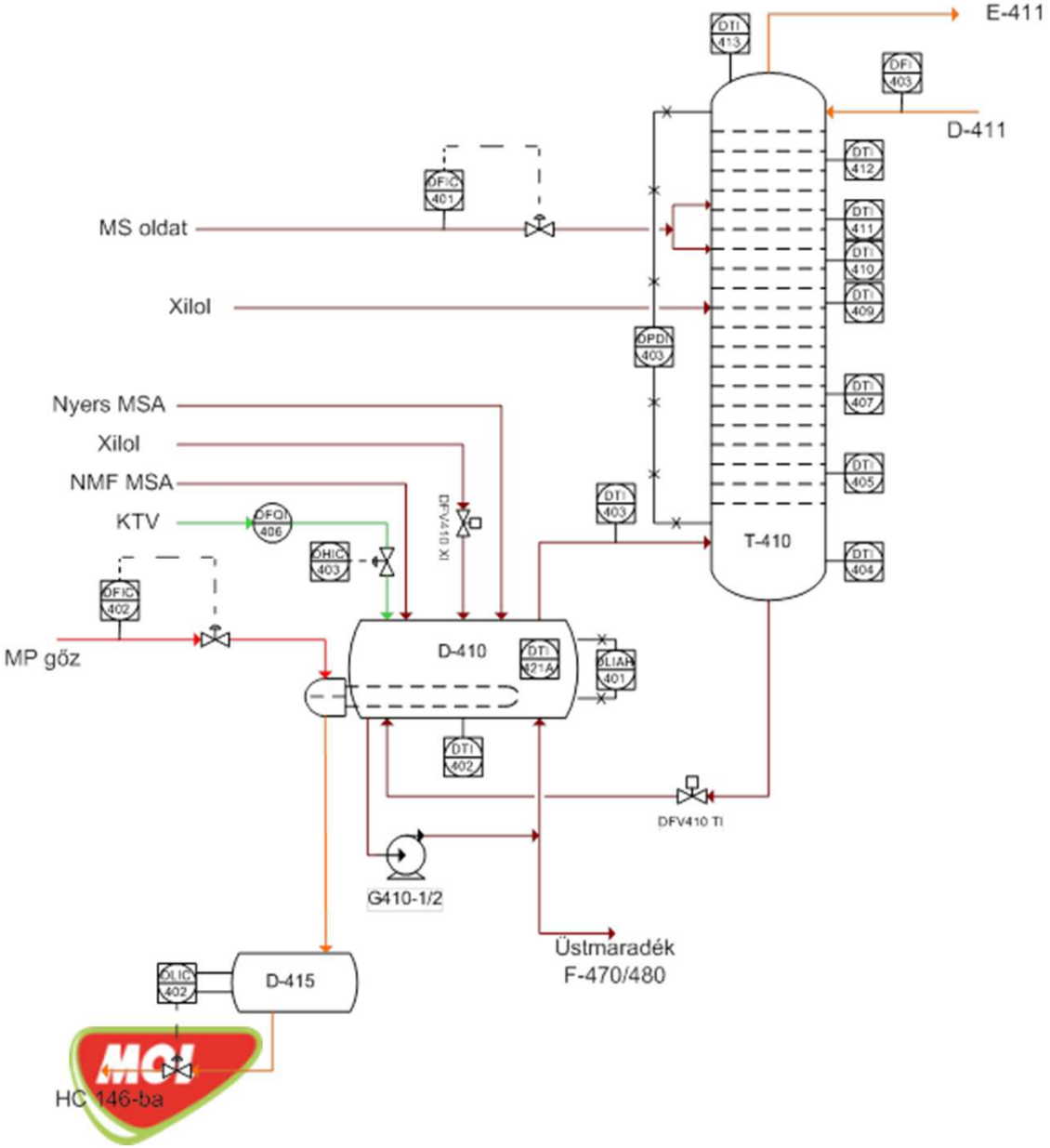


In order to avoid droplets in off gas there is a mesh grid on absorber top

Absorber contains 10 trays

MAn technology

Technology units: Azeotrope distillation



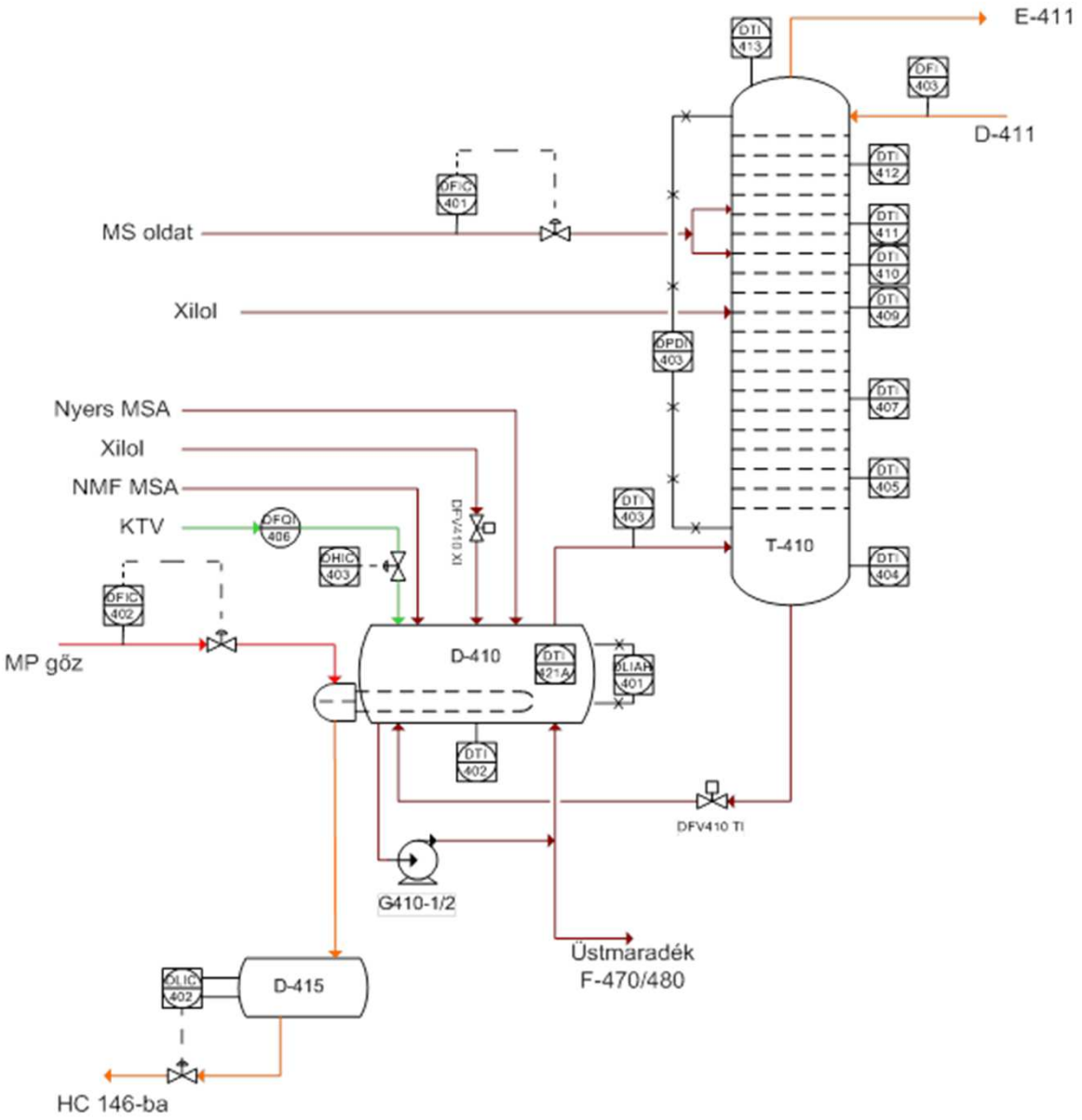
The distillation is not continuous but batch process and consists of several steps:

- **Feedstock:** 42 w% MA solution
- **Xylene loading:** Approximately 30 m^3 of xylene mixture is loaded into the refining kettle, with orthophosphoric acid (to prevent MAn decomposition). *Xylene loading can also be done on tray 13 of the column (MAn backwash)*
- **Heating**: Heating with medium-pressure steam to 138°C at the column head temperature, circulation starts (D410-T410-E411-D411-T410-D410).
- **Raw MAn loading:** Loading 10-50 m^3 of raw MSA from the raw MSA tank
- **Dehydration:** Increase steam heating to 18-20 m3/h total xylene reflux. If the temperature stabilizes, introduce the MA solution into the column. The dehydration of the MS solution takes place in the area below the feed tray at ~150°C (dehydration zone). Here, MA releases physically and chemically bound water to the upward-moving xylene vapours, and xylene reflux absorbs the MAn."

MAn technology

Technology units: Azeotrope distillation

- **Xylene withdrawal:** Vacuum production by using ejector. The system pressure reduction till 465 mbarg and withdraw the Xylene to Xylene tank.
- **Pre-distillate withdrawal:** after xylene withdrawal, the product stream is transferred to the raw MAn tank (165 °C, 200 mbar). Heating adjustment (reflux rate: 5) until on spec product quality. Sampling every half an hour.
- **Main distillate withdrawal:** if quality is adequate, the material flow should be switched to the product MAn tank.
- **Post distillate withdrawal:** vacuum leakage. Discharge of product and reflux line into the raw MAn tank after the product flow has ceased.
- **Emptying the refining kettle emptying, aqueous distillation:** dilution of boiler water in the cauldron, then pushing the resulting material into a tank.

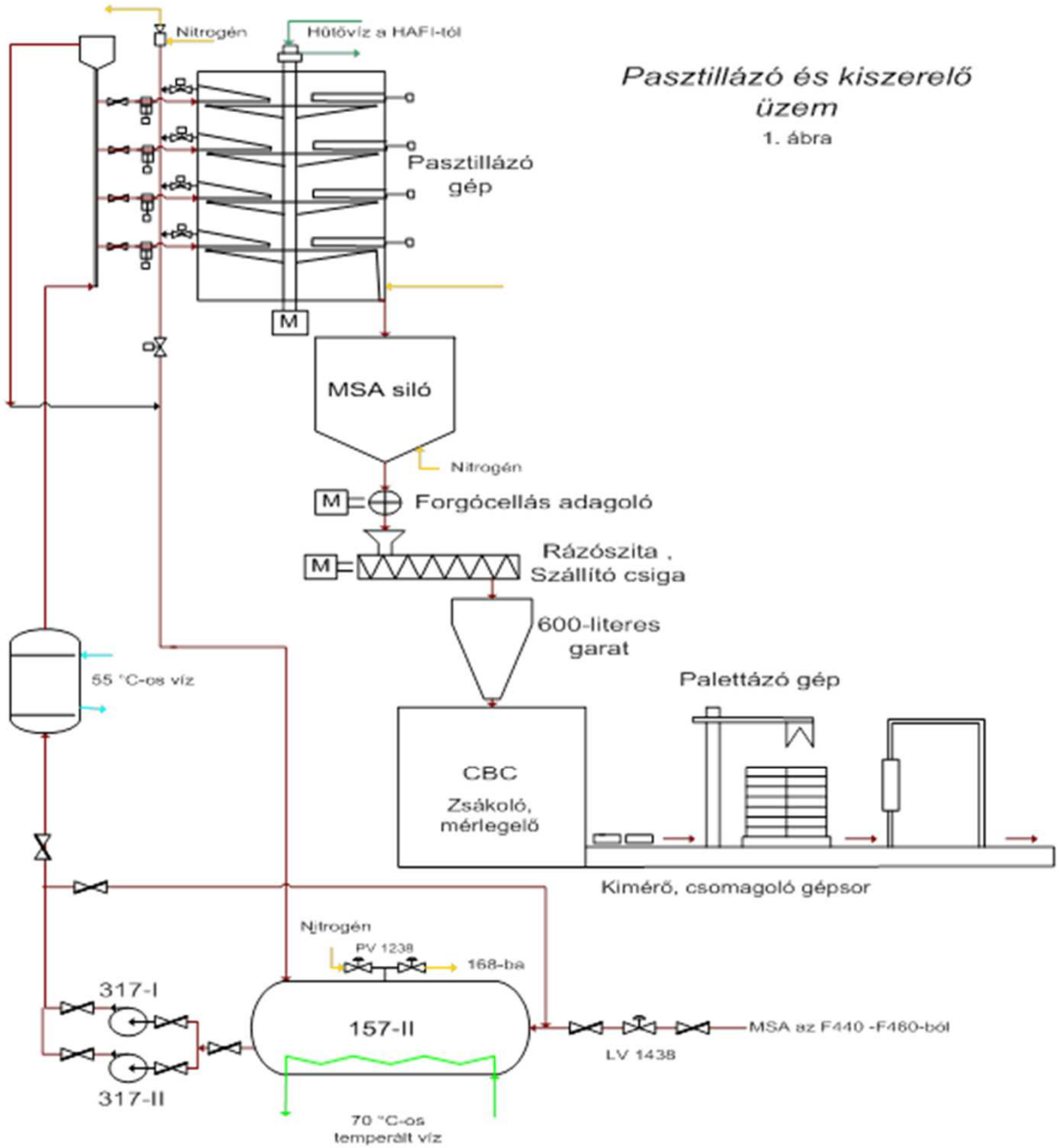


MAn technology

Technology units: Pastille production

Parts of the technology:

- **Tableting machine:** The MSA enters the machine at a temperature close to pour point.
- **MSA silo**: It is used to store the tableted product.
- **Cell dispenser**: transfers the MSA tablets from the silo to the dispensing line.
- **Shaking sieve:** its function is to separate the powder.
- **Bagging**: the solid MSA is transferred into 25 kg bags.
- **Robot palletiser**: the robot arm places the bags on the pallet. The robot palletises the bags.
- **Rotary arm stretch wrapper**: Watertight wrapping



MAn technology

Technology units: Pastille production

MAn technology
Technology units: Others

- Neutralisation of acidic waters
  - Acidic water entering the neutralisation tanks is neutralised by adding a 40% NaOH solution to the set pH 7-8.
  - The neutralised waters are sent to the biological treatment plant
- Treatment of residual sludge
- Thermal off gas incinerator
  - The off gas leaving the absorber still contains combustible hydrocarbons in the order of a few tenths of a percent, which cannot be released to the air. The task of the final gas incinerator is to destroy these harmful substances.
  - The destruction process also produces steam in this part of the plant.

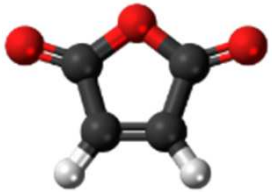
MAn product
General features

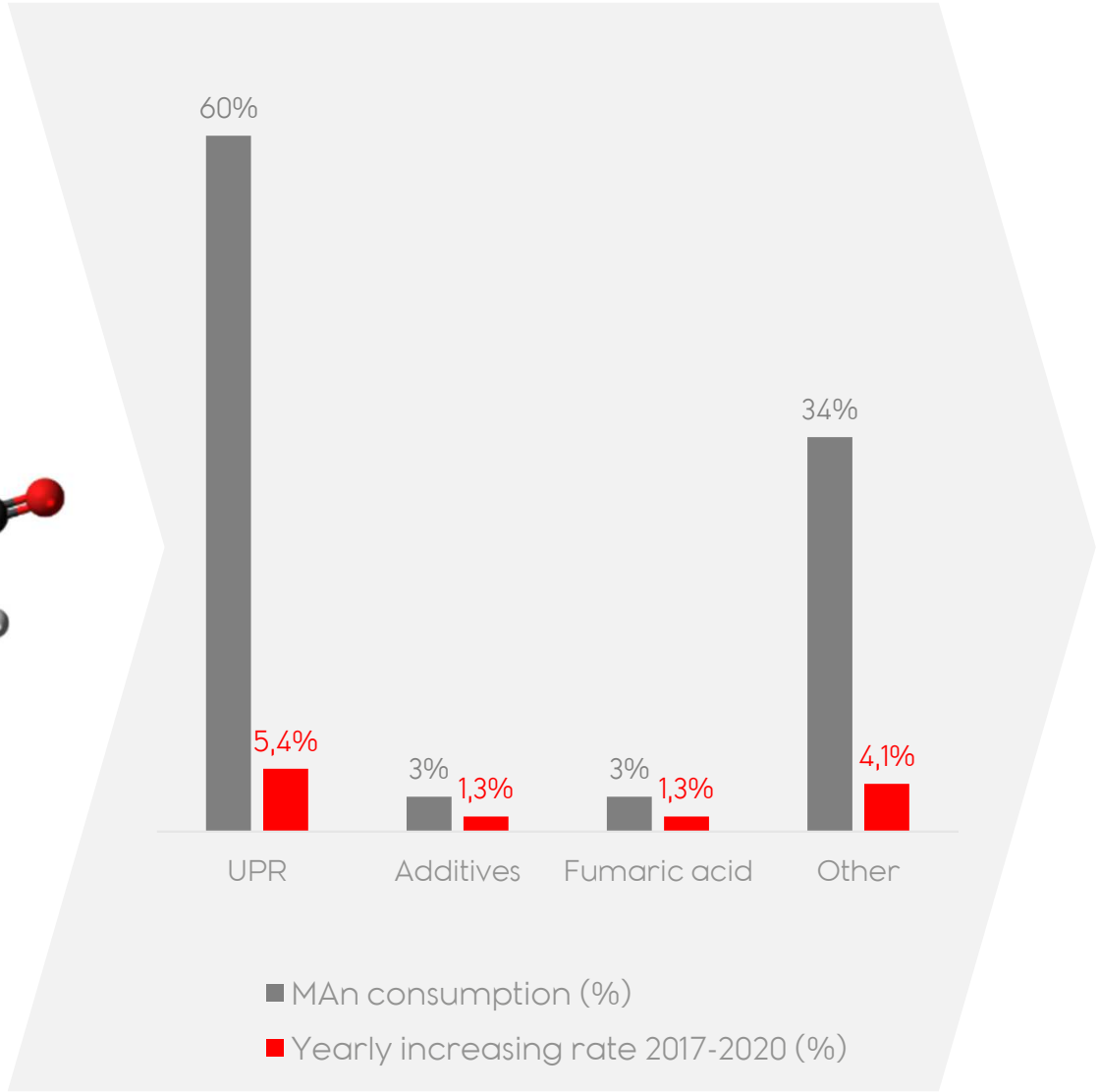
- Quality control in an accredited laboratory
- Continuous quality control seven days a week
- Online testing methods (raw material, product)
- Liquid and Paste MAn tests

Tulajdonság	Előírás
Kémiai jelölés	C4H2O3
MSA tartalom, legalább %	99,5
Dermedéspont, °C minimum	52,3
Forráspont, °C	202
Olvadáspont, °C	53
HAZEN szín, maximum	20
Hamutartalom, maximum, m/m%	0,002
Vastartalom, legfeljebb, ppm	2
Maleinsav tartalom, legfeljebb, %	3
Külső megjelenés	Fehér, kristályos

MAn product
General features

MAn product
How to use?





UPR production

Additives

Food industry

Pharmaceuticals

Plastics

Paints

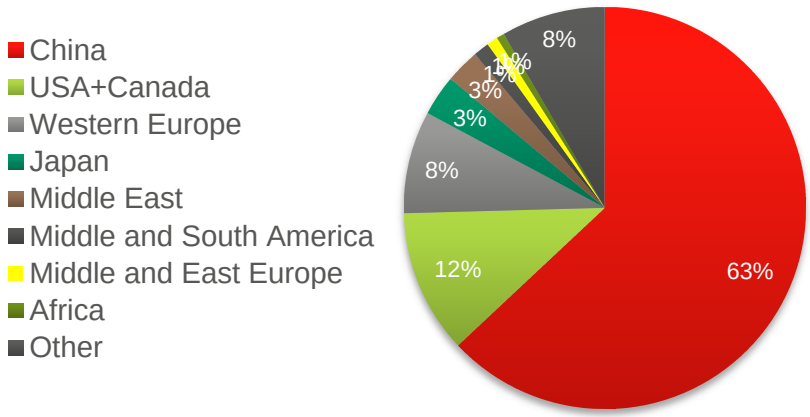
Surfactants

Pesticides

MAn market conditions

Global capacity of MAn production (2018)

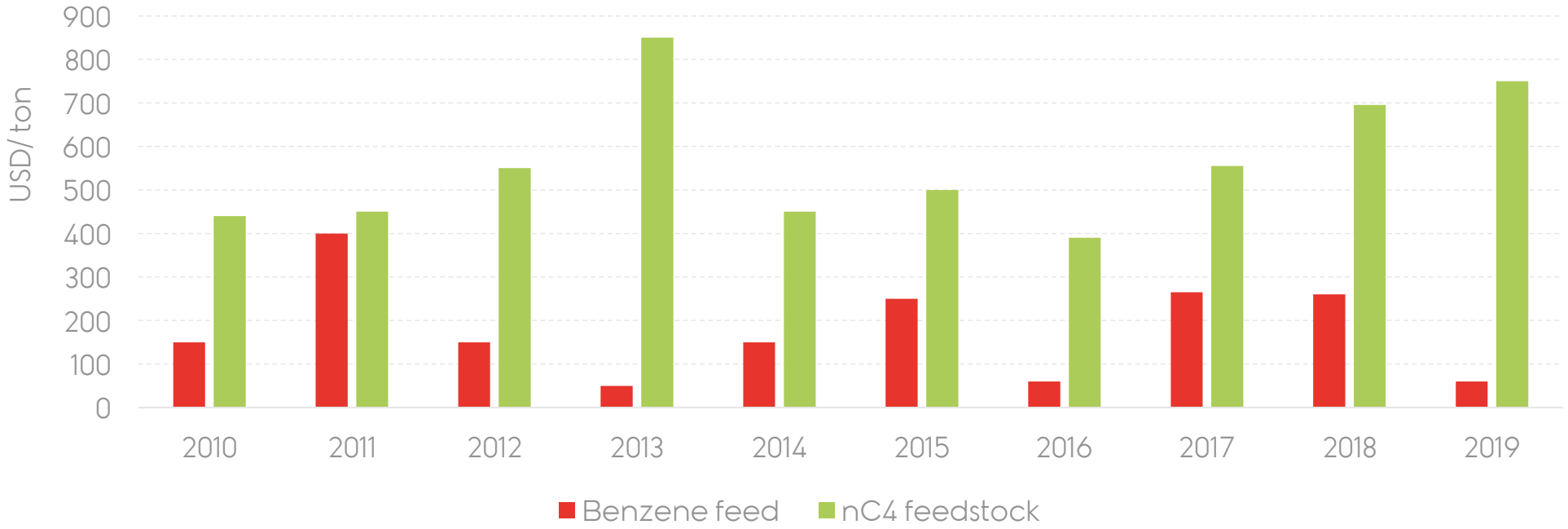
	Company	Location	Capacity, ktpa	Percentage of world capacity, %
1.	Huntsman Corporation	USA	207.5	6.6
2.	Zibo Qixiang Chemical	China	200	6.4
3.	Qiaoyou Chemical	China	128	4.1
4.	Changzou Chemical	China	120	3.8
5.	Sinopec fibers	China	120	3.8
6.	Polynt	Italy	101	3.2
7.	Ningbo Chemical	China	100	3.2
8.	Tianjin Zhong Chemical	China	100	3.2
9.	International Diol Company	Saudi Arabia	85	2.7
10.	LANXESS	USA	73	2.3
…	MOL Hungary	Hungary	22	0.7



- The global installed MAn capacity is 3 122 kt/year. The TOP 10 manufacturers represent the 39% of total world capacities
- China alone has a capacity of 1967 kt/year, representing 63% of installed capacity of the world.
- If the MSA development has been realised, the Danube Refinery will account for ~1.4% of total capacity.

MAn market conditions

Margins from Benzene and nC4

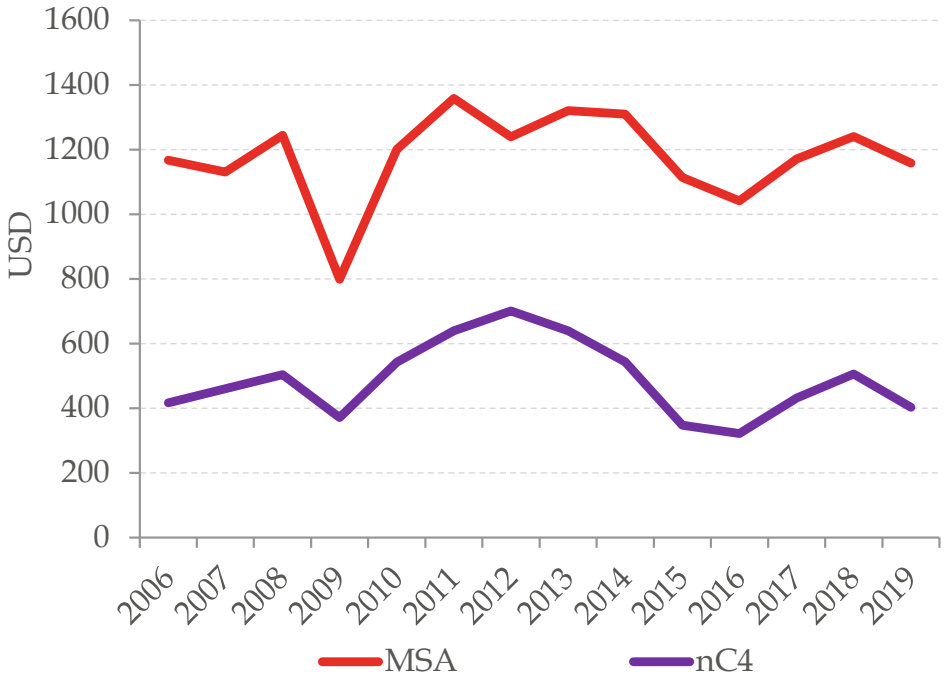


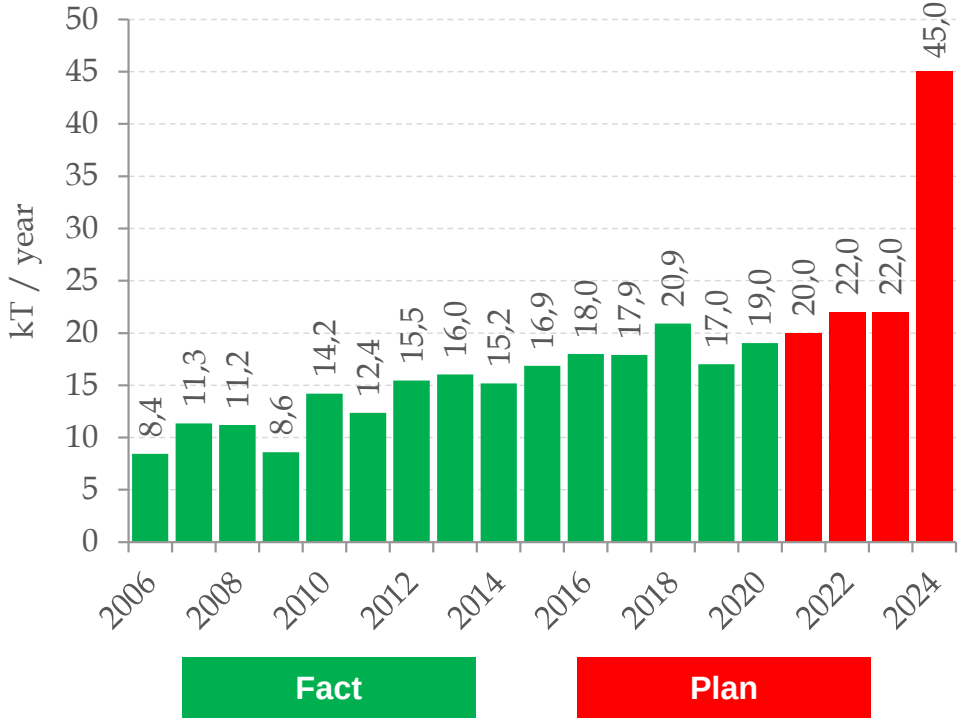
- Benzene as a feedstock for MSA is increasingly taking a back seat. Nowadays, MSA production from benzene is mainly done in Asia.
- On average, the margin for MSA produced from normal butane is seven times higher than for benzene feedstock.

MAn market conditions

Margins from Benzene and nC4

- Among refinery products, MSA has one of the highest prices.
- The price difference between the nC4 feedstock and the MSA product is ~500-700 EUR. Feedstock and product prices vary with the world oil price, but the difference is roughly constant.
- As the market condition and future prospects for MSA are very good, further capacity additions is in progress



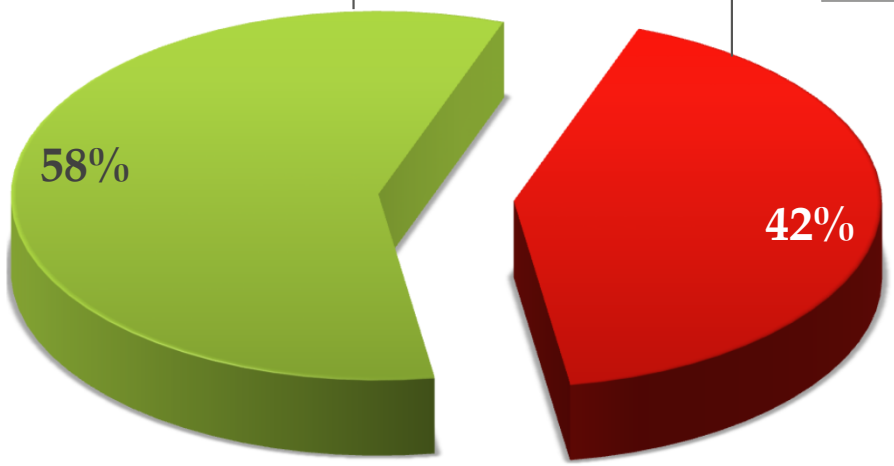


Energy consumption

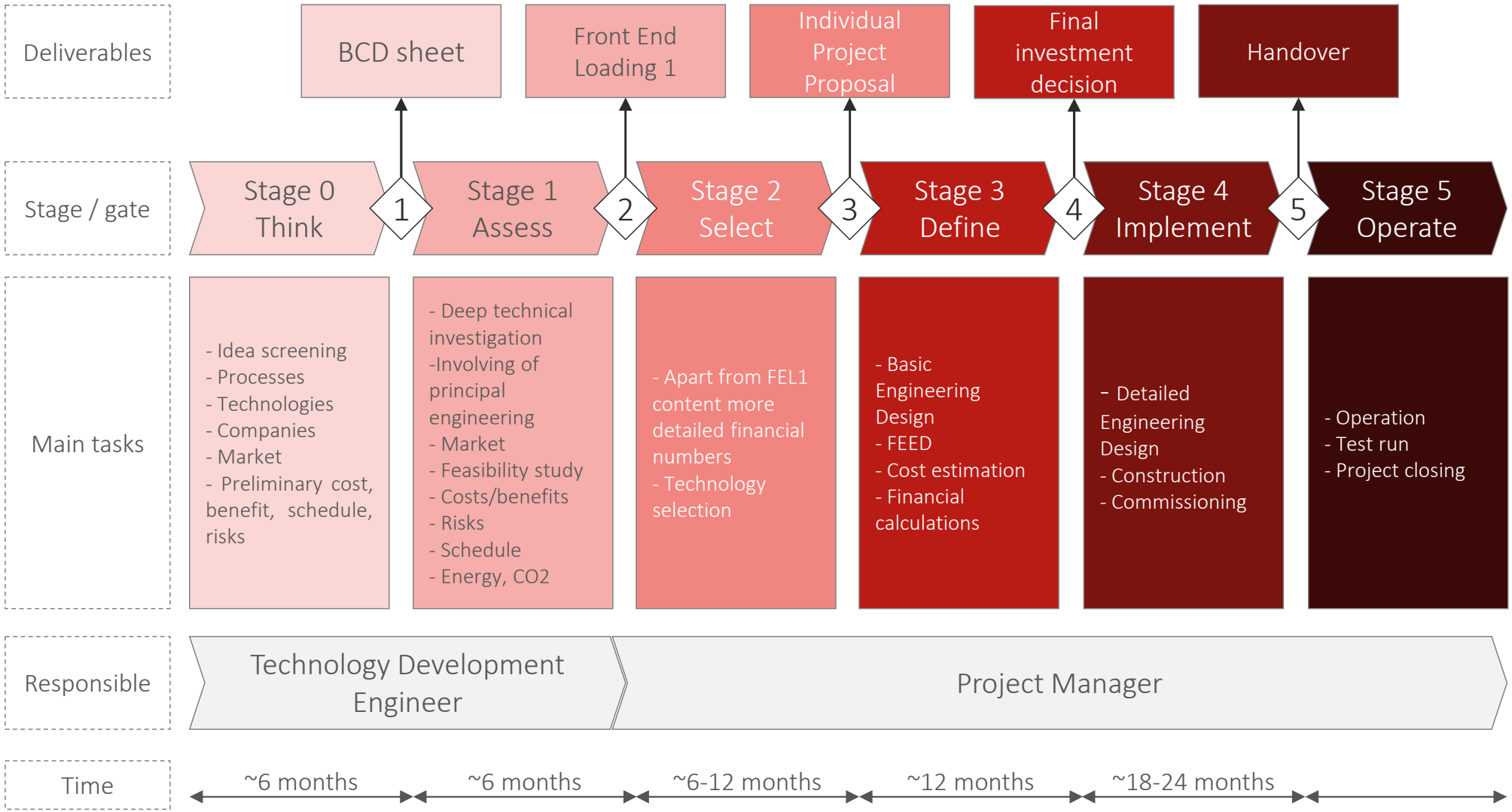
- Although MAn is a large energy consumer, it has a positive energy balance because it produces large amounts of steam from the heat generated during the processes.
- "Green" steam means lower CO2 intensity (Fit for 55)

Energy	Volume
Steam production	1170 TJ
CO2	-80 ktpa

Energy	Volume
Natural gas	-460 TJ
Steam	-260 TJ
Electricity	-110 TJ
CO2	58 ktpa



Classic project flowchart



Did you know?

Annual water consumption of MAn unit is:

~2 million m^3

600 swimming pool (50 meters) can be loaded

Annual electricity consumption of MAn unit is:

30 GWh

Annual electricity consumption of 175 thousand households

Hourly NG consumption of the MAn unit is:

1500 Nm^3

Average amount of natural gas used per household in ~one year

Annual air consumption of MAn unit is:

3,5 million Nm^3

Enough to load 1400 hot air balloons