Hydrocarbon Processing

– Desuphurisation
– Diesel quality improvement

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BME
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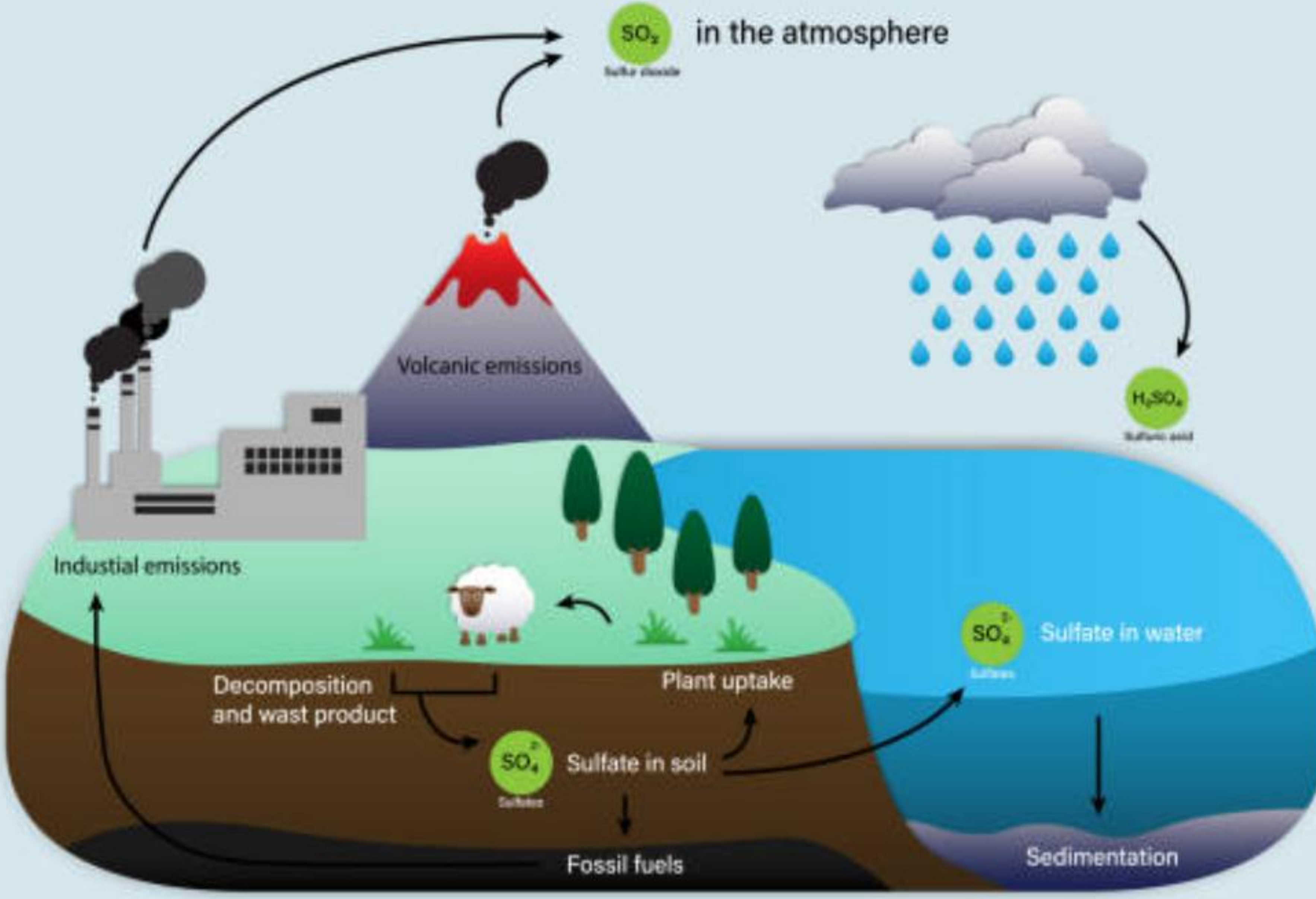
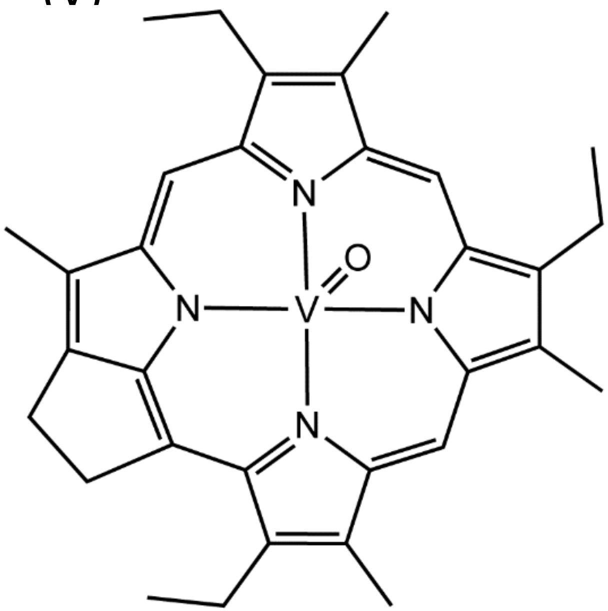
Sulfur Cycle



Composition: types of **impurities**

- **Heteroatom** components
  - **Sulphur compounds**
    - Elemental sulphur
    - Hydrogen sulphide
    - Mercaptanes
    - Sulphides-disulphides
    - Thiophen and derivatives
  - **Nitrogen compounds**
    - Amines
    - Nitriles
    - Pirrols
  - **Oxygen compounds**
    - Organic acids
    - Phenols
- **Inorganic ions**
  - Solved in the dissolved water
  - Na^+, Cl^-, HCO_3^-, etc.
- **Organic metal complexes**
  - Mainly nickel (Ni) and vanadium (V)

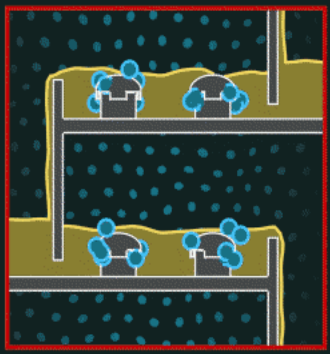


DISTILLATION

Crude oil contains a variety of **hydrocarbons** that have different boiling points. To separate these compounds, the oil is first sent to a boiler where it is heated into a super-hot mixture of liquid and vapour called the feed.

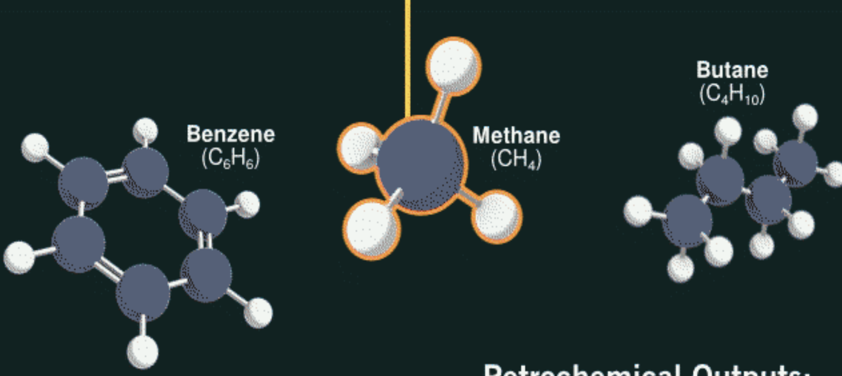
The mixture is then fed into a **distillation tower.** In here, the compounds with a lower boiling point rise up as vapours, while the compounds with a higher boiling point fall downwards as liquids.

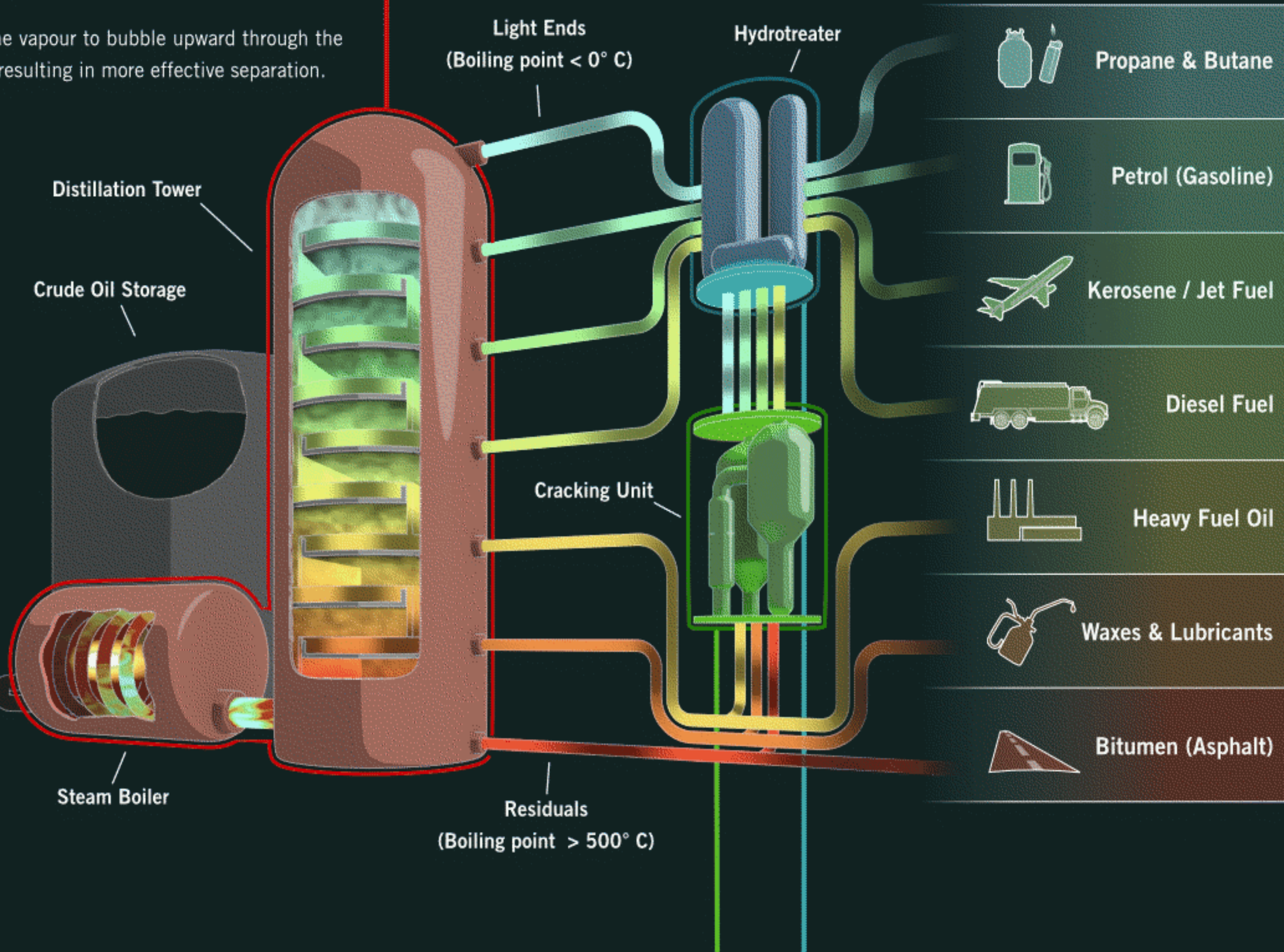
The tower contains trays that allow the vapour to bubble upward through the liquid, helping to exchange heat and resulting in more effective separation.



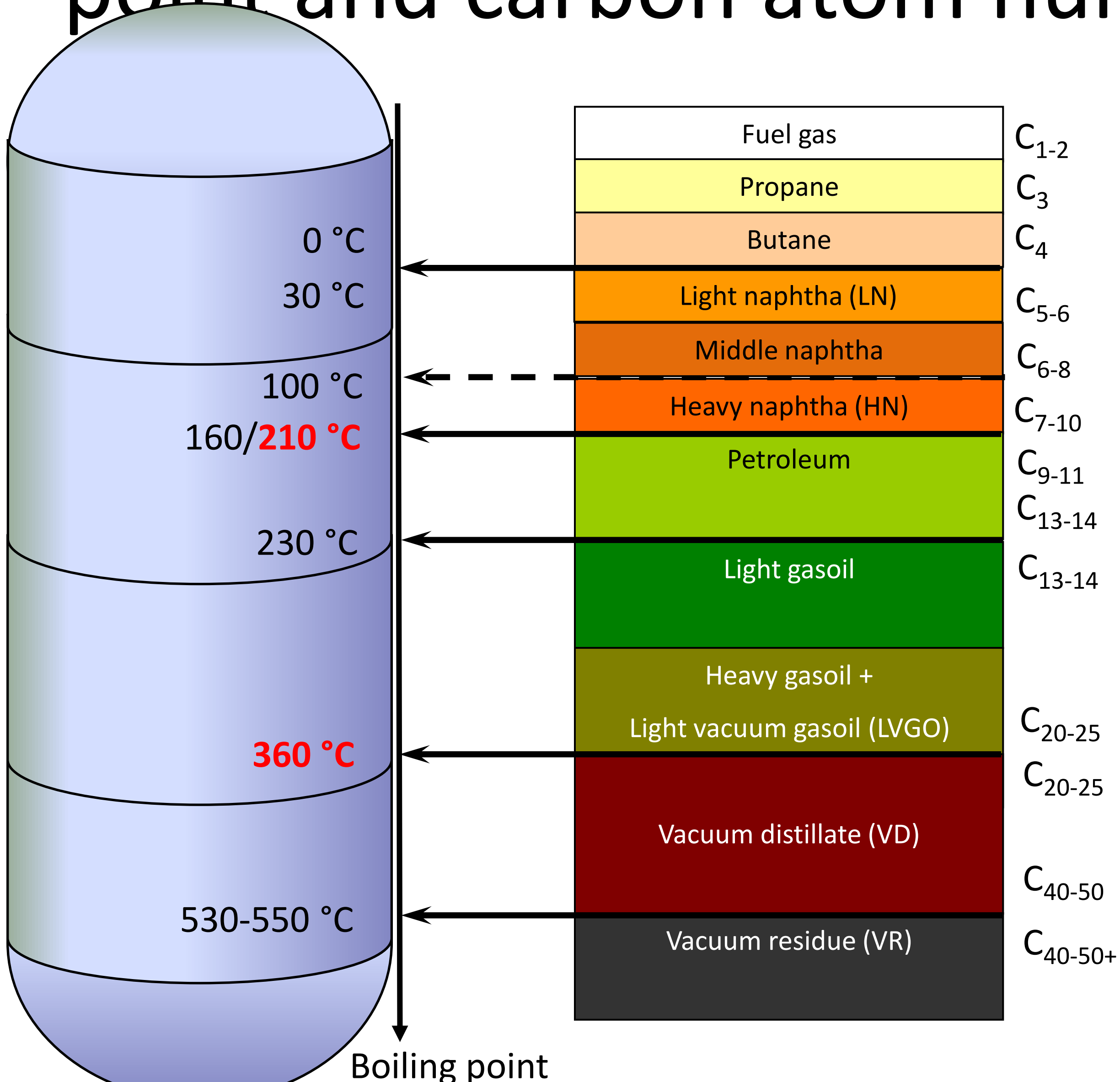
The distilled products are then piped off from the different levels of the tower. These separated products are called **fractions** or **distillates.**

This process may take place along multiple distillation towers.





Crude oil fractions according to boiling point and carbon atom number



1. Desulphurization

Importance of desulphurisation

- To meet **product quality specification**
  - Gasoline, diesel: 10 ppm S content
- To prevent **catalyst poisoning** during downstream processing
  - pl. catalytic reforming (CCR): platinum catalyst
- To prevent **corrosion**
  - Carbon steal equipment, heat exchanger protection
- To protect **exhaust gas catalyst** in cars
  - Platinum catalyst as well as CCR
- General **environment, health protection**
  - Acidic rain, etc.

Desulphurisation of **fuel gas**

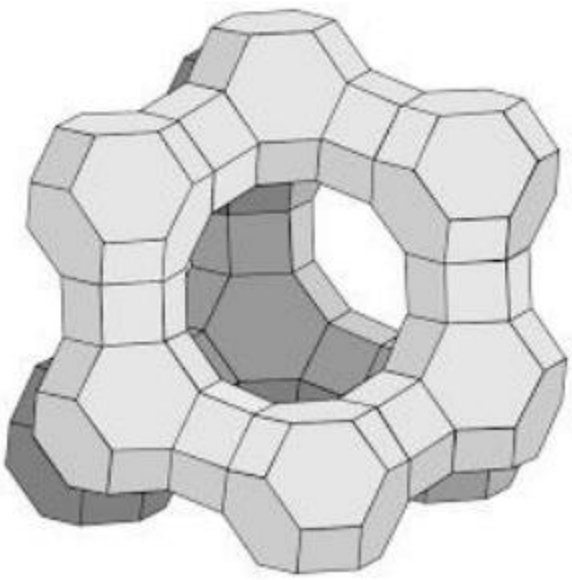
- **Definition:** fuel gases are the gaseous intermediate streams produced during crude oil processing, which consists basically only methane and ethane components
- Their **marketisation is not economic** (low amount, expensive to separate), therefore they are used internally in furnaces (burning)
- **Principle** of desulphurisation: gas/liquid extraction (amine washing)
  - Absorption – desorption
  - **Absorbents**: ethanol-amines
  - Deatils later under the title „sulphur recovery”

LPG **desulphurisation**

- **LPG:** Liquified Petroleum Gases
- Examples of **sulphur species** in LPG
  - Carbonil-suphide (COS; bp.: -50°C)
  - Methyl-mercapthan (CH_3SH; bp.: +6°C)
- **Technologies**
  - Removal with molecular sieves
    - **straight-run LPG** (straight-run: stream from the primary distillation)
  - Removal with caustic
    - Cracked, **olefinic LPG**

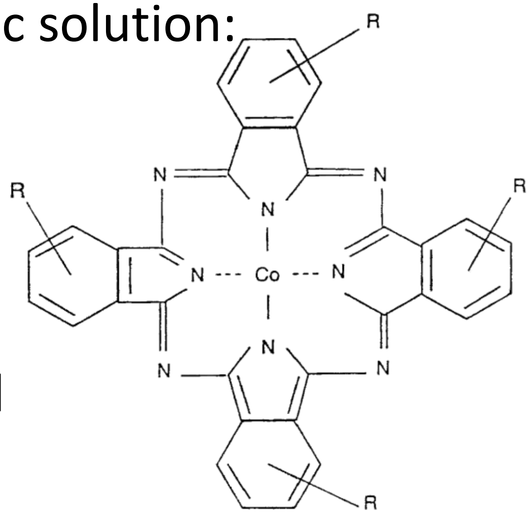
LPG desulphurisation with **molecular sieves**

- **Theory** of desulphurisation: adsorption (liquid/solid extraction)
- **Advantage:** simple operation, cheap adsorbent
- **Disadvantage:** not good for olefinic fractions
- Molecular sieves used as adsorbent
  - eg. ***13X***, 5A zeolites
  - Molecular sieves: strictly regular pore size mineral

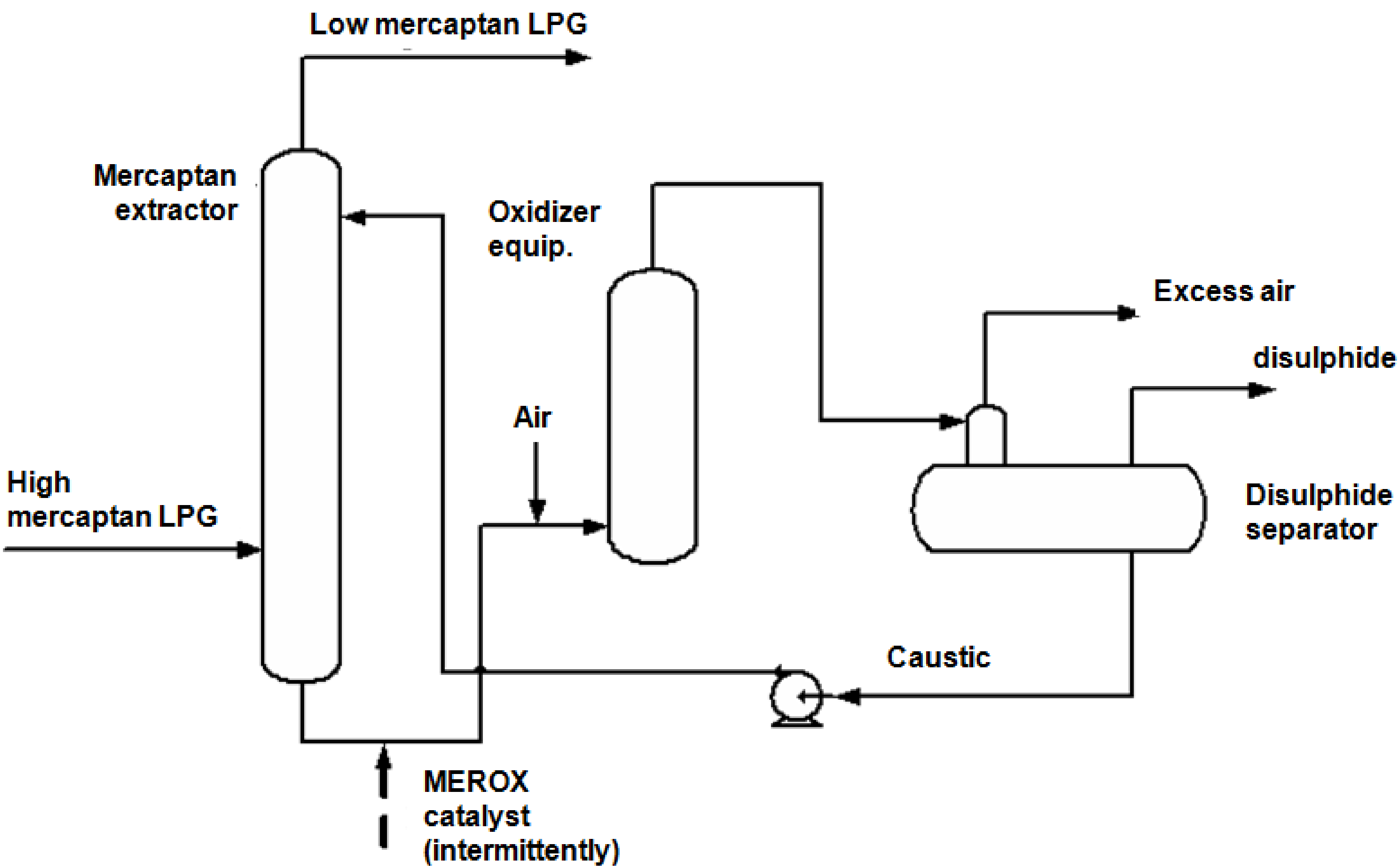


LPG desulphurisation with **caustic**

- Two step, homogeneous catalytic process, conventionally called **„MEROX process"**
- **Advantage:** good for olefinic fractions (LPG from FCC, DCU)
- **Disadvantage:** caustic, catalyst containing waste water is produced
- 1. step: **desulphurisation**
  - **Theory:** absorption (liquid/liquid extraction)
  - Acidic mercapthanes are captured with caustic solution:
    - *($H_2S + 2NaOH \rightarrow Na_2S + 2H_2O$)*
    - $RSH + NaOH \rightarrow RSNa + H_2O$
- 2. step: **caustic regeneration**
  - **theory**: homogeneous catalytic oxidation
  - ***Cobalt-ftalocianin*** catalyst complex used to oxidise the mecapthanes into disulphides and regeneration of caustic
    - *($2Na_2S + 4H_2O + 2O_2 \rightarrow Na_2S_2O_3 + 2NaOH + 3H_2O$)*
    - $2RSNa + \frac{1}{2}O_2 + 2H_2O \rightarrow RSSR + 2NaOH + H_2O$



Flowscheme of the **MEROX process**

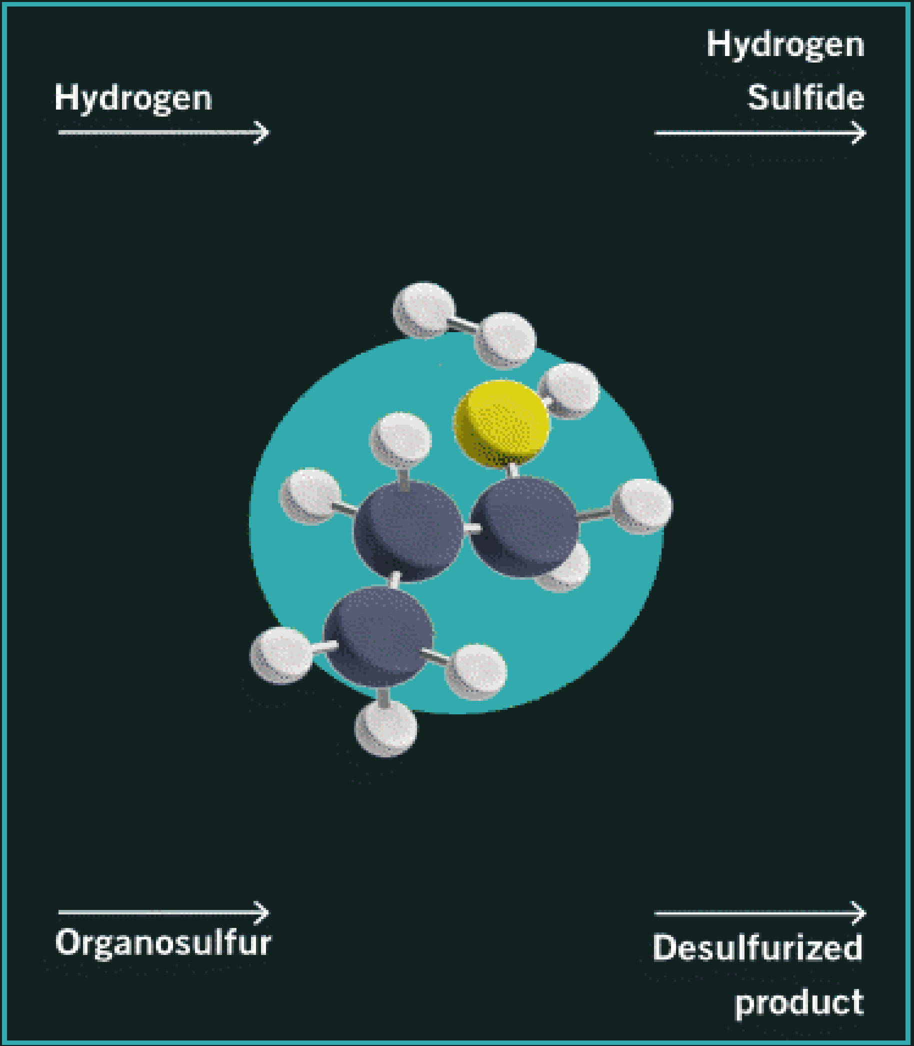


Hydrotreatment of straight-run liquid fractions

Hydrotreatment **of straight-run liquid fractions**

- **Theory:** heterogeneous catalytic desulphurisation
- **Similar** technologyis used to desulphururised gasoline, petroleum, gasoil and vacuum distillate
- Good for straight-run **and** cracked streams
- Difference is in the **process parameters**
- Process needs **huge amount hydrogen** (in pure form)
  - Hydrogen plant (SMR-PSA)
  - Catalytic reformer (hydrogen is a byproduct here)

HYDROTREATING

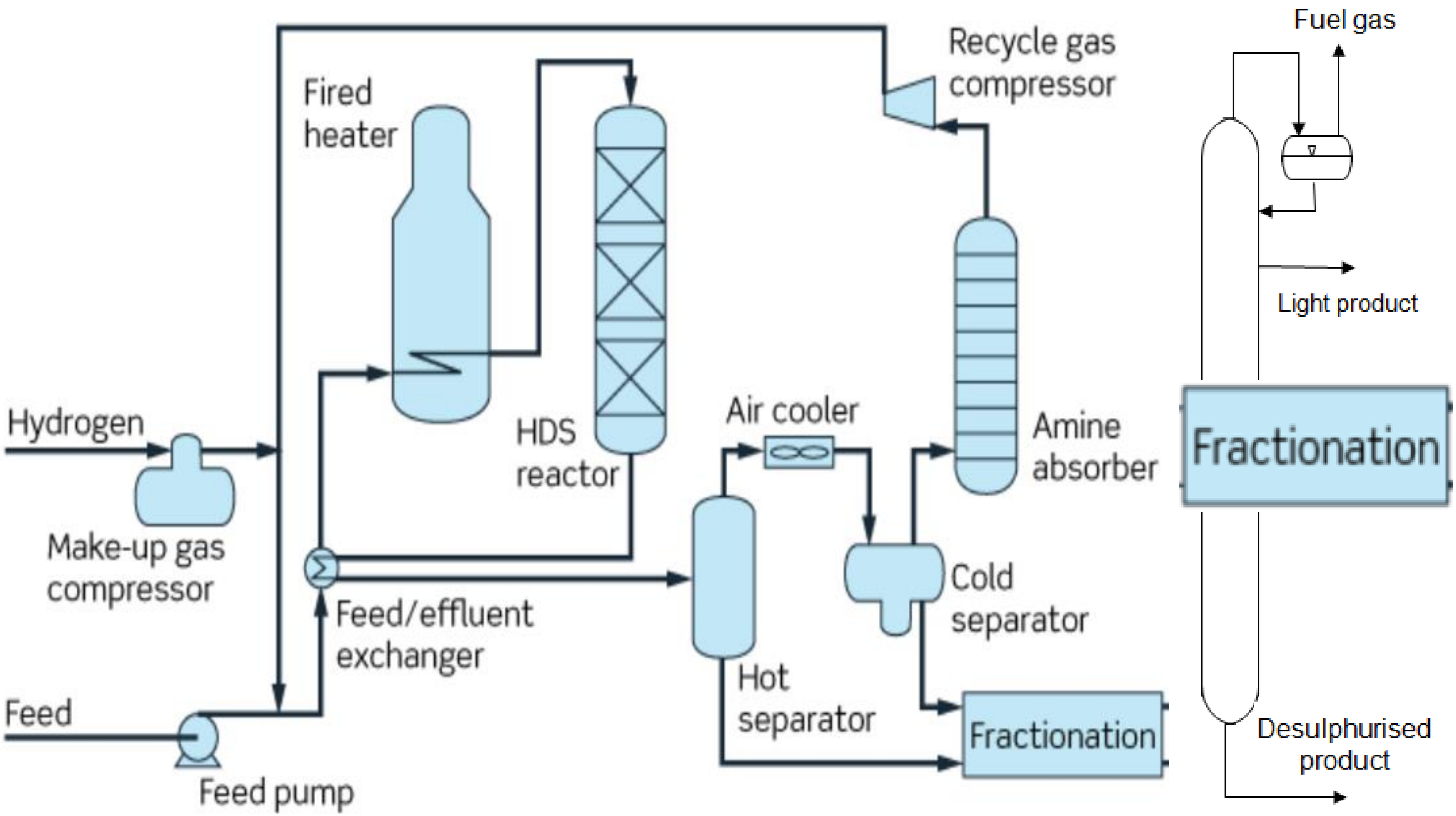


The distilled product may still contain undesirable elements, the most important of which is **sulfur.** Fuels containing sulfur, when burned, produce pungent sulfur dioxide.

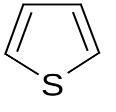
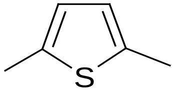
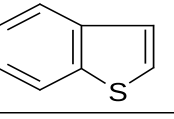
Hydrotreating removes sulfur by exposing the product to hydrogen gas as well as extreme heat and a catalyst. The hydrogen atoms bond with the sulfur, converting it into **hydrogen sulfide**. This hydrogen sulphide gas can then be removed via re-distillation.

In this example, the organosulfur compound **propanethiol** (C_3H_8S) is being converted into cleaner-burning **propane** (C_3H_8).

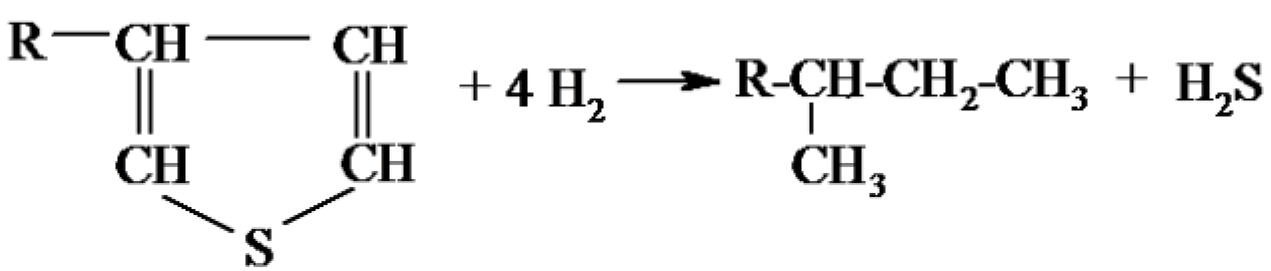
Flowscheme of the **hydrotreaters**



Sulphuric species of gasolines

Compound	Formula	Boiling Point, °C
Mercaptans		
ethyl-mercaptan	C_2H_5SH	35,0
n-nonyl-mercaptan	$C_9H_{19}SH$	220
Sulphides		
dimethyl-sulphide	CH_3-S-CH_3	38
n-butyl-sulphide	C_4H_9-S- C_4H_9	188
Disulphides		
dimethyl-disulphide	CH_3-S-S-CH_3	109
ethyl-disulphide	C_2H_5-S-S- C_2H_5	153
Thiophenes		
thiophene		80
dimethyl-thiophene		135
benzothiophene		221

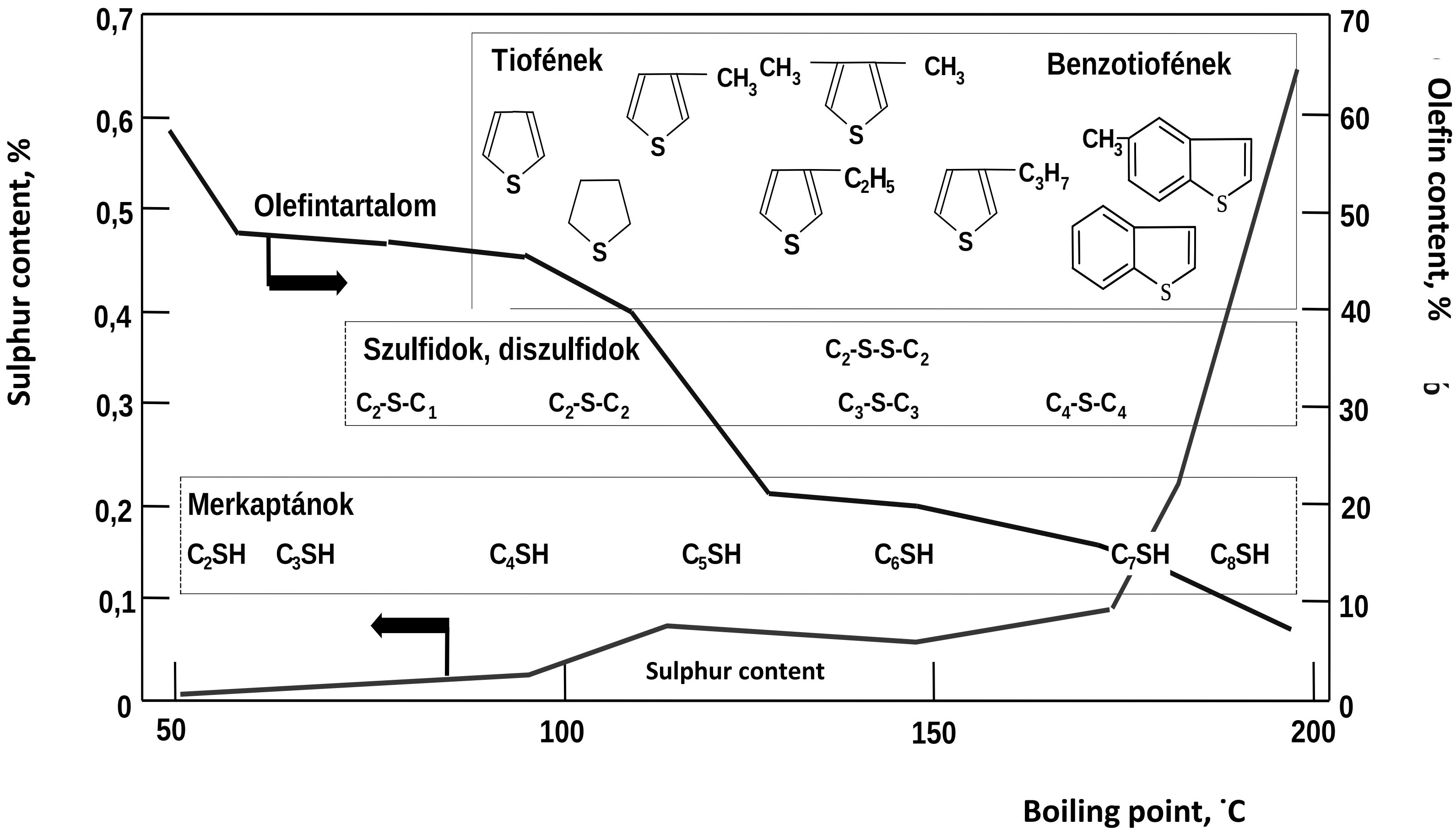
Example reactions of **gasoline desulphurisation**

- **Mercaphanes**:
  - $R\text{-}SH + H_2 \rightarrow R\text{-}H + H_2S$
- **Disulphides:**
  - $R_1\text{-}S\text{-}S\text{-}R_2 + 3H_2 \rightarrow R_1\text{-}H + R_2\text{-}H + 2H_2S$
- **Tiophenes:**
  - 

Challanges of cracked feed streams

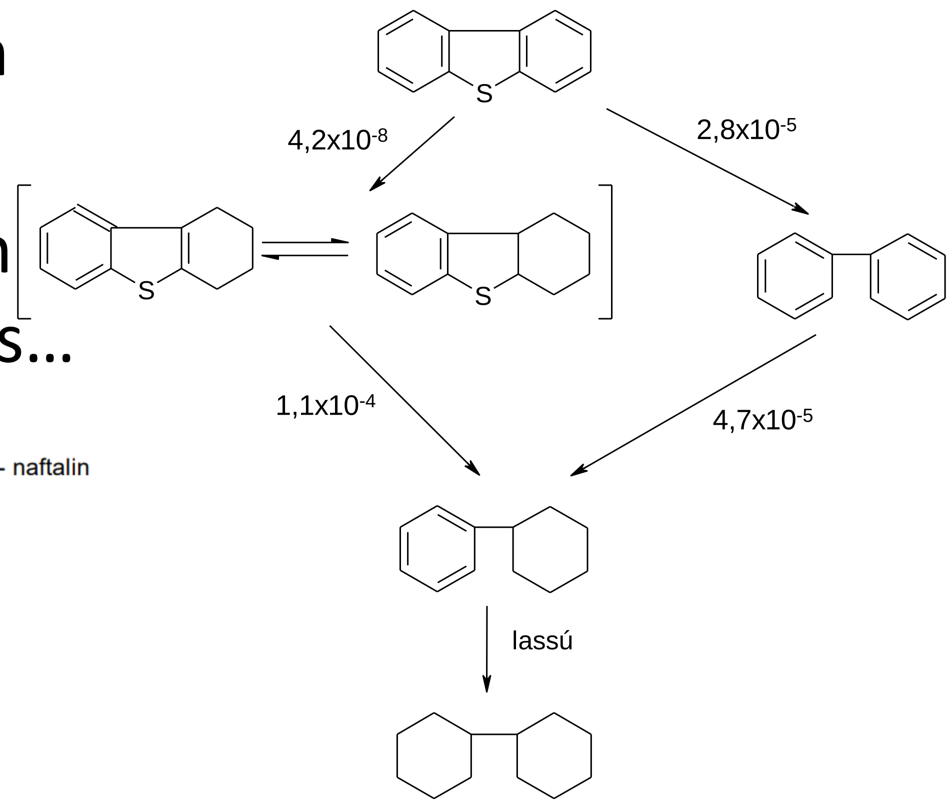
- **Potential feed stream**
  - Cracked (FCC) gasoline (appropriate RON – big quantity)
  - Coker (DCU) gasoline (not appropriate RON – medium quantity)
  - Pyrolysis gasoline (acetylenes present – small quantity)
- **Main challenge:** minimalization of olefine saturation
  - Olefines are high RON components
  - RON loss minimalization
  - Polymerization behavior of acetylenes are outstanding, during storage, they cause gum deposition problems (antioxidation additives are helpful)
- **Solutions**
  - Acetylene-selective hydrogenation
  - Fractionation and hydrogenation of heavier fraction only
  - Mild reaction conditions

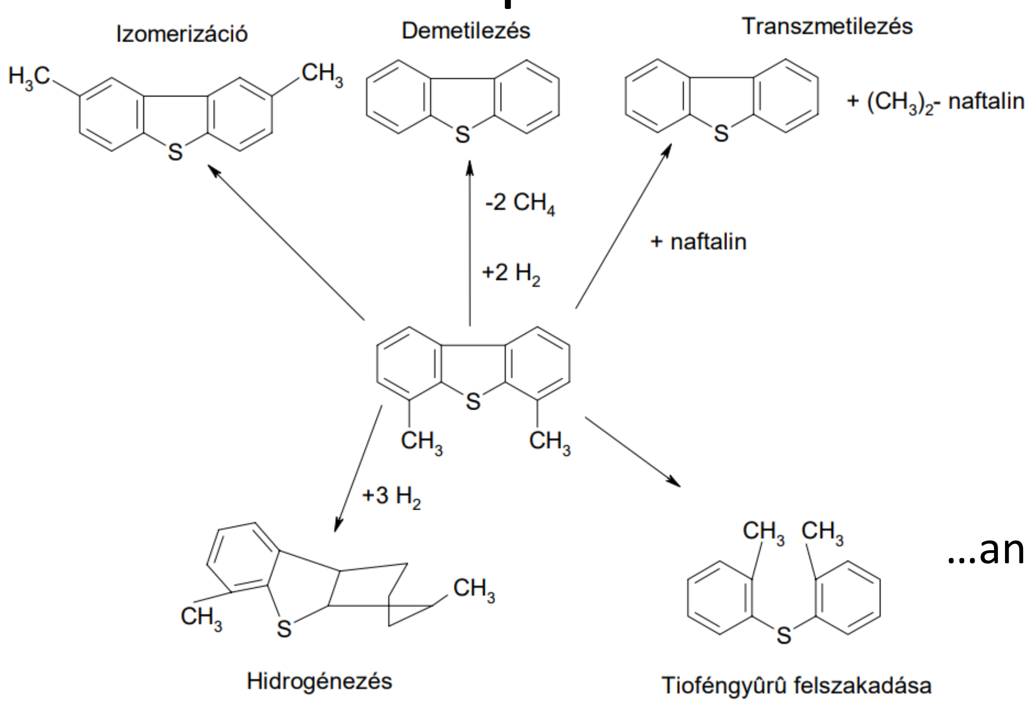
Typical composition of FCC gasoline



Hydrotreatment of **petroleum and gasoil** fractions

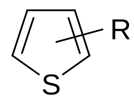
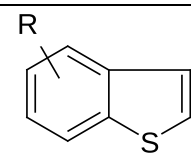
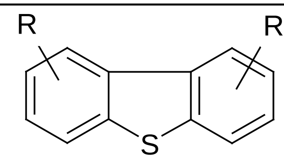
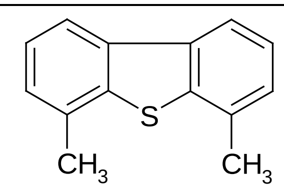
- For desulphurization of simple sulphur compounds see gasoline desulphurisation
- Dibenzo-thiophen desulphurisation reaction web with speed constants…





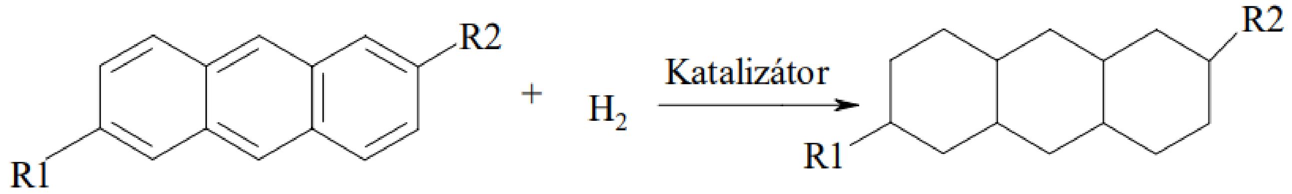
…and the alternative reaction routes during sterically hindered dialkyl-dibenzo-thiophenes desulphurisation

Relative reactivity of tiophene derivatives

Sulphur compound	Formula	Relative reactivity
Thiophenes		1
Benzothiophenes		0,6
Dibenzothiophenes		0,04
4- and/or 6-methyl-dibenzothiphene		0,004

Hetereoatom removal of petroleum and gasoil fractions

- **Nitrogen** removal reactions:
  - Amines, nitriles, pirrol-derivatives, pyridine-derivatives:
    - pl. $C_{18}H_{37}NH_2 + H_2 \rightarrow C_{18}H_{38} + NH_3$
    - In general: ammonia and saturated hydrocarbons are formed
- **Oxygen** removal reaction:
  - Phenol-derivatives, ketones, furane-derivatives, carboxyl-acids:
    - In general: water and saturated hydrocarbons are formed
- **Additional reactions:**
  - Aromatic ring saturation (mainly multiple-ring aromatics)

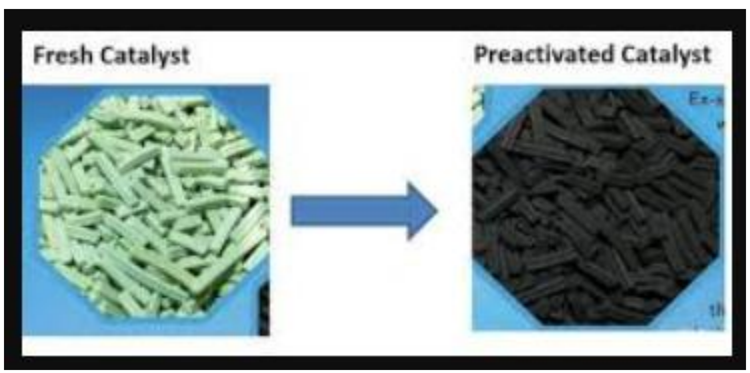


Typical data of straight-run liquid fractions hydrotreatment

Feed	Gasoline	Petroleum	LAGO	HAGO	LVGO
Parameters:					
TBP cut points, °C	70-200	160-240	240-350	300-380	350-550
Sulphur, % (mg/kg)	(100-1000)	0,1-0,4	0,2-2	0,5-3	1-4
Process parameters:					
Temperature, °C	310-330	330-350	340-360	350-380	360-380
Pressure, bar	20-30	20-35	35-60	70-80	70-90
LHSV, h^{-1}	4,0-6,0	2,0-4,0	1,0-3,0	0,8-2,0	0,5-2
H_2/feed ratio, vol/vol	100-150	150-200	200-250	250-300	300-400
Product sulphur, mg/kg	<1	<1-50	≤10-50	≤10-500	≤50-500
Catalyst cycle life, month	48	→	→	→	24
Relative catalyst cost, 1/t	1	1,2	1,2	2	3,6

Hydrotreating catalysts

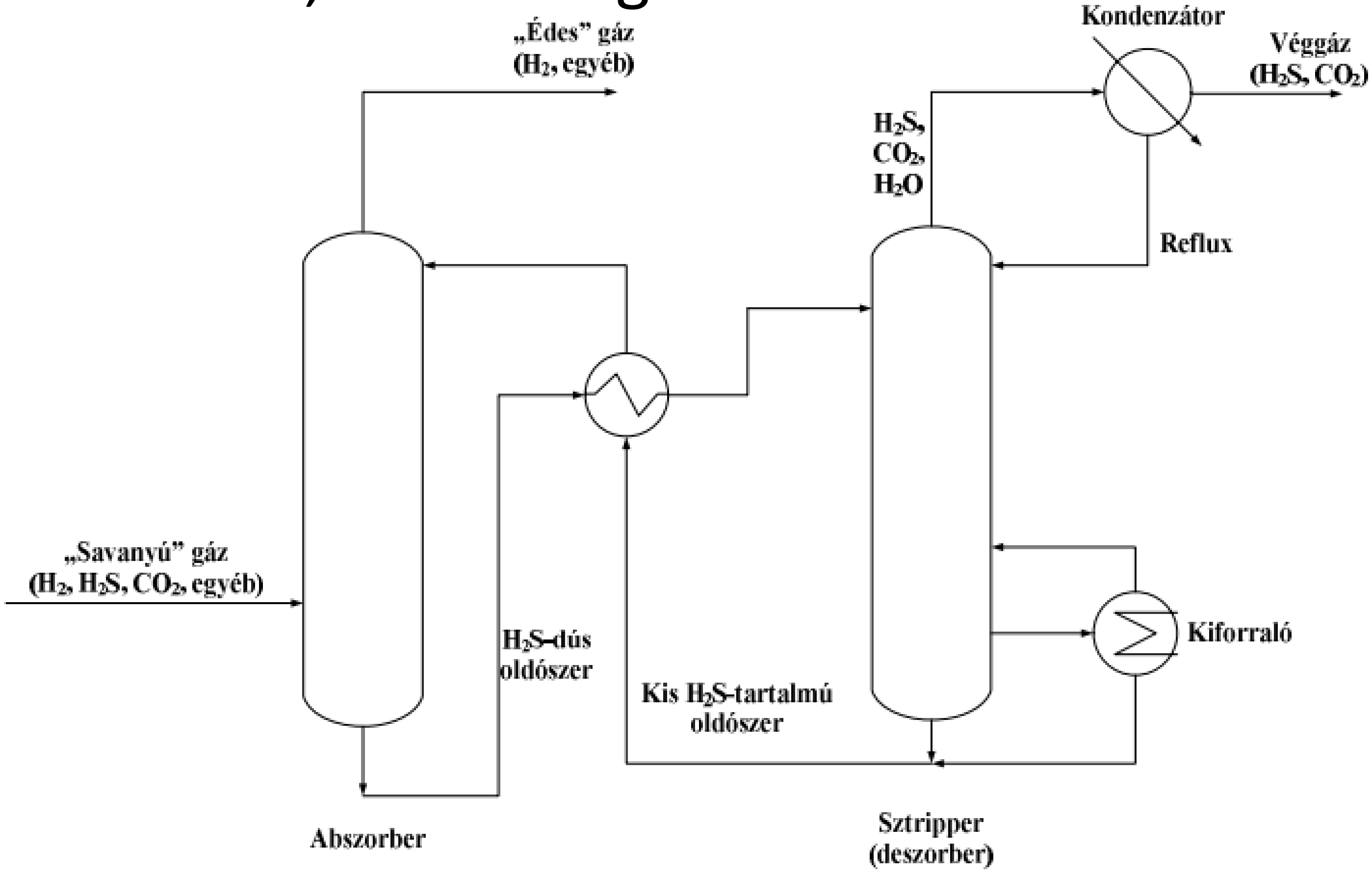
- Catalyst consists typically
  - Transition metals: Ni, Co, Mo
  - On metal-oxid support: aluminium-oxide
  - Active in sulphide form
  - eg. **$CoMo/Al_2O_3$, $NiMo/Al_2O_3$**



2. Sulphur removal and production from hydrogene-sulphide containing gases

Hydrogene-sulphide removal from gas mixtures

- **Theory:** gas/liquid extraction
- **Feedstock:** fuel gas, H_2S rich gases from hydrotreaters, FCC sour gas



Used **absorbents**

- **Chemisorption reaction on MDEA:**
  - $(HO\text{-}CH_2\text{-}CH_2)_2\text{-}N\text{-}CH_3 + H_2S \longrightarrow ((HO\text{-}CH_2\text{-}CH_2)_2\text{-}N\text{-}CH_3)^+(SH)^-$

Oldószer	MEA	DEA	MDEA
Molekulatömeg	61	105	119
Koncentráció (tf%)	15	30	50
Minimális H_2S terhelés (n_{H2S}/n_{amin})	0,05	0,02	0,01
Maximális H_2S terhelés (n_{H2S}/n_{amin})	0,6	0,6	0,5
Kapacitás (H_2S/dm^3)	1,77	2,18	2,77

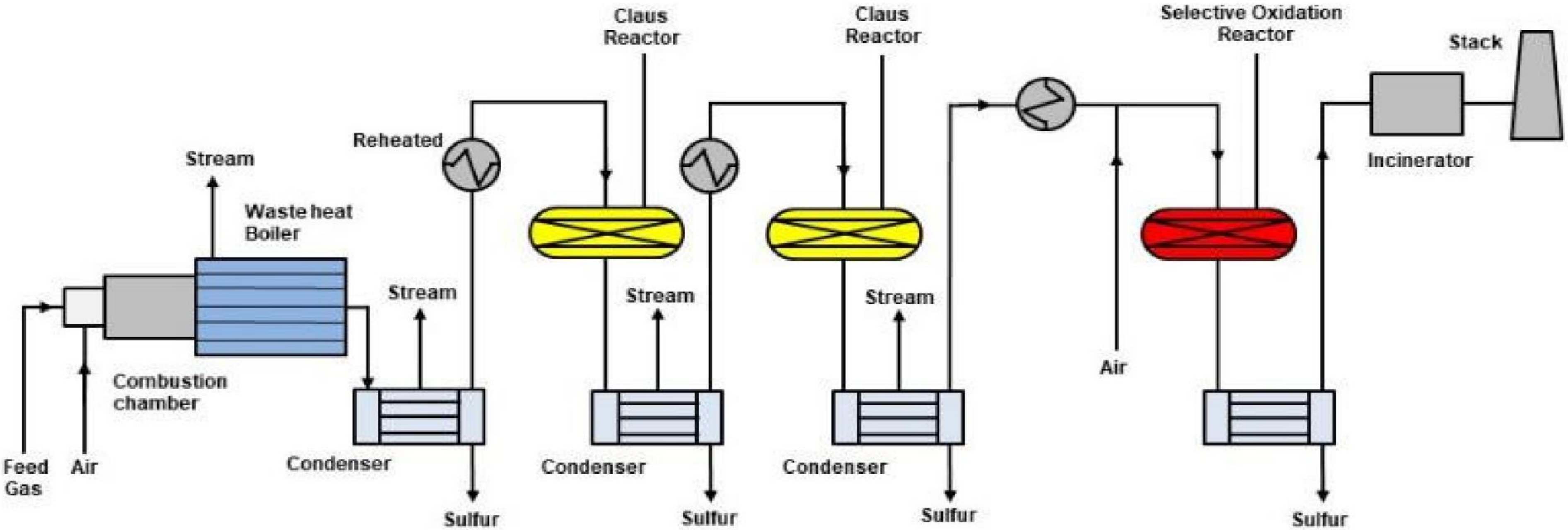
MEA: mono-etanol-amin
DEA: di-etanol-amin
MDEA: metil-di-etanol-amin

Sulphur production from hydrogen-sulphide – the **Claus process**

- **Theory:**
  - 1. step: **partial oxidation** (stochiometric 1/3)
  - 2. step: **catalytic conversion**
  - Conversion **efficiency:** 99,5% <
- **Reactions:**

(1) Részleges égés az égetőkamrában	$H_2S + 1,5O_2 \rightarrow SO_2 + H_2O$
vagy (az elégetlen H2S-t is figyelembe véve)	$3H_2S + 1,5O_2 \rightarrow 2H_2S + SO_2 + H_2O$
(2) Claus reakció az égetőkamrában és a katalitikus konverterben	$2H_2S + SO_2 \rightarrow 3S + 2H_2O$
(1+2) Bruttó reakció	$2H_2S + O_2 \rightarrow S_2 + 2H_2O$

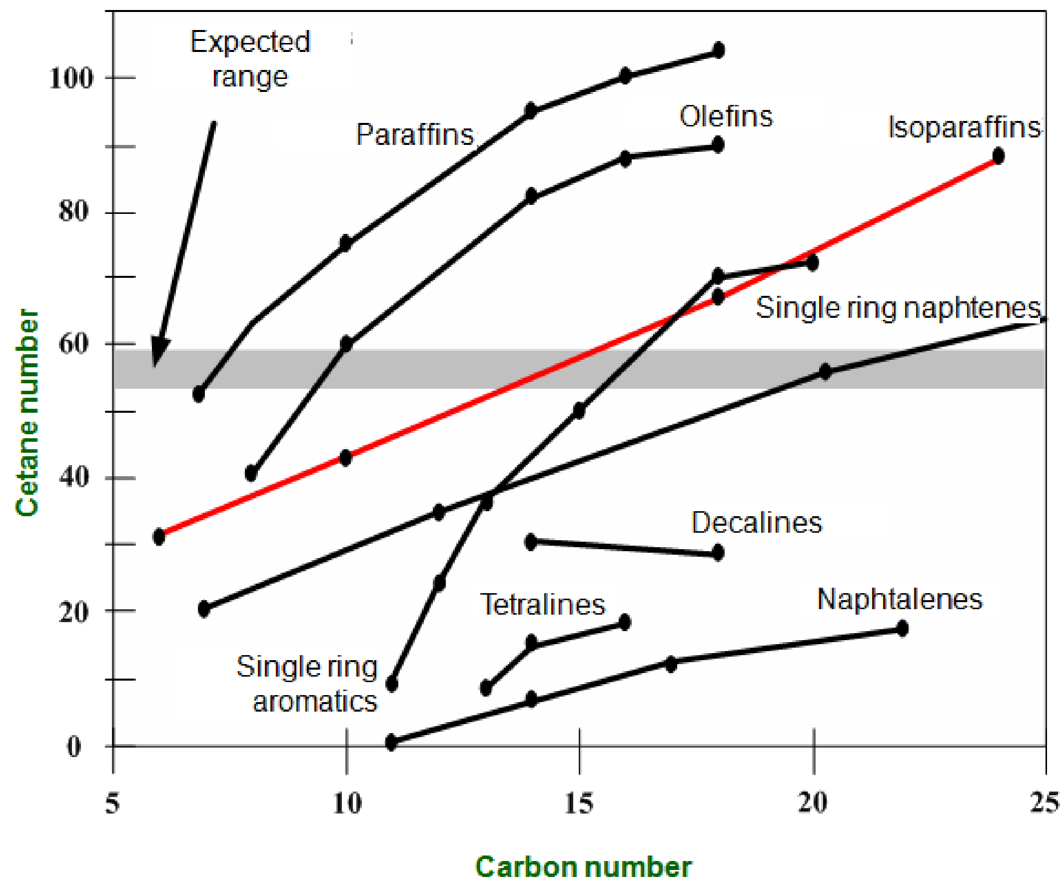
Flowscheme of the Claus process



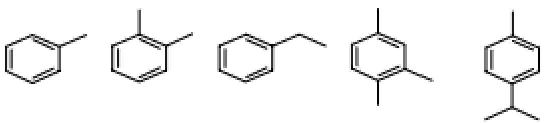
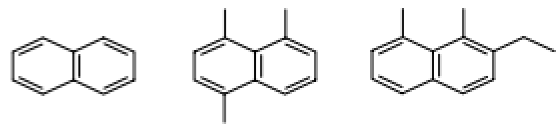
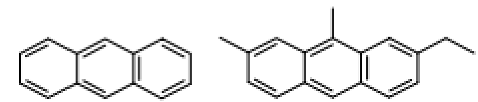
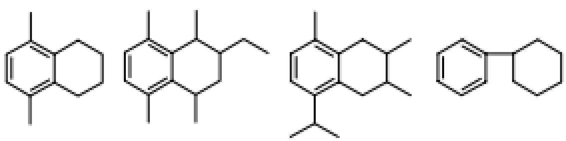
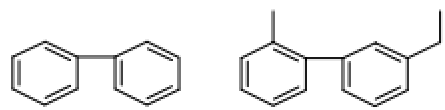
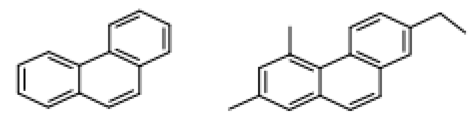
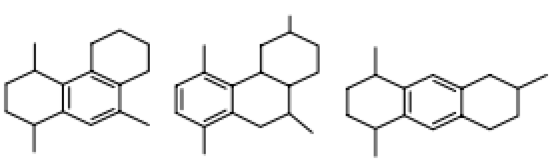
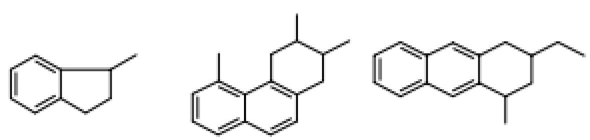
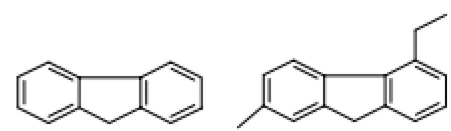
3. Quality improvement of gasoil fractions

A. **Aromatic saturation** of gasoils

- Goal of aromatic saturation
  - **Cetane number** of the polyaromatic molecules are low:
    – cetane number of gasoil increases with saturation
  - Burning of polyaromatic molecules are **not complete**
    – with saturation the particulate emission may be decreased (older diesel cars exhaus gas)



Some exampes of polyaromatic molecules

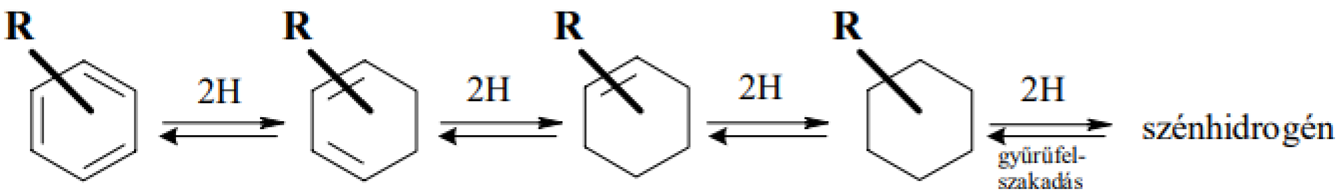
Egy-gyűrűs aromások	**Kétgyűrűs aromások**	**Háromgyűrűs aromások**
- alkil-benzolok 	**- naftalinok és alkil-naftalinok** 	**- antracének** 
- benzo-cikloparaffinok 	**- bifenilek** 	**- fenantrének** 
-benzo-dicikloparaffinok 	**- nafténaromások (indének)** 	**- fluorének** 

Saturation of aromatic hydrocarbons

Erősen exoterm reakció

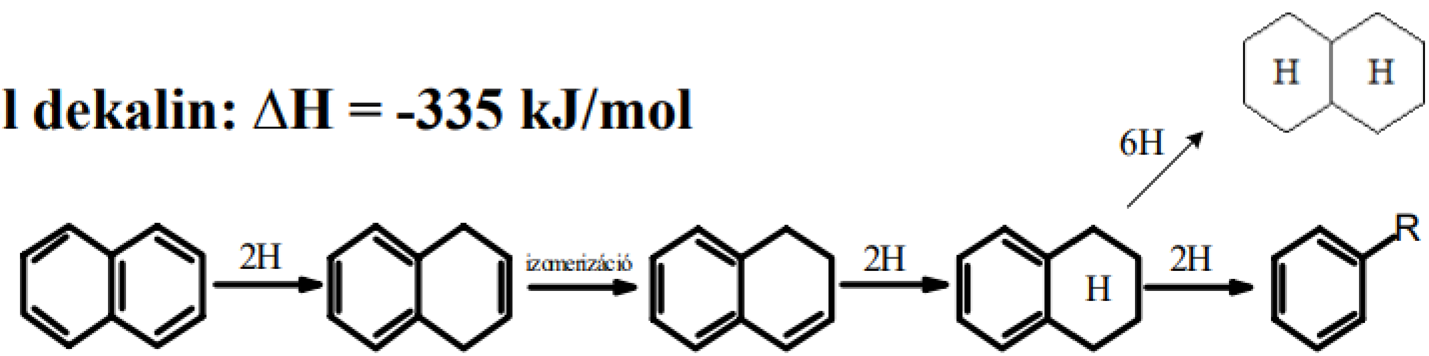
- **alkil-benzolból alkil-ciklohexán:**

toluol → metil-ciklohexán: ΔH = -205 kJ/mol
etil-benzol → etil-ciklohexán : ΔH = -202 kJ/mol
kumol → 2-ciklohexil-propán: : ΔH = -184 kJ/mol

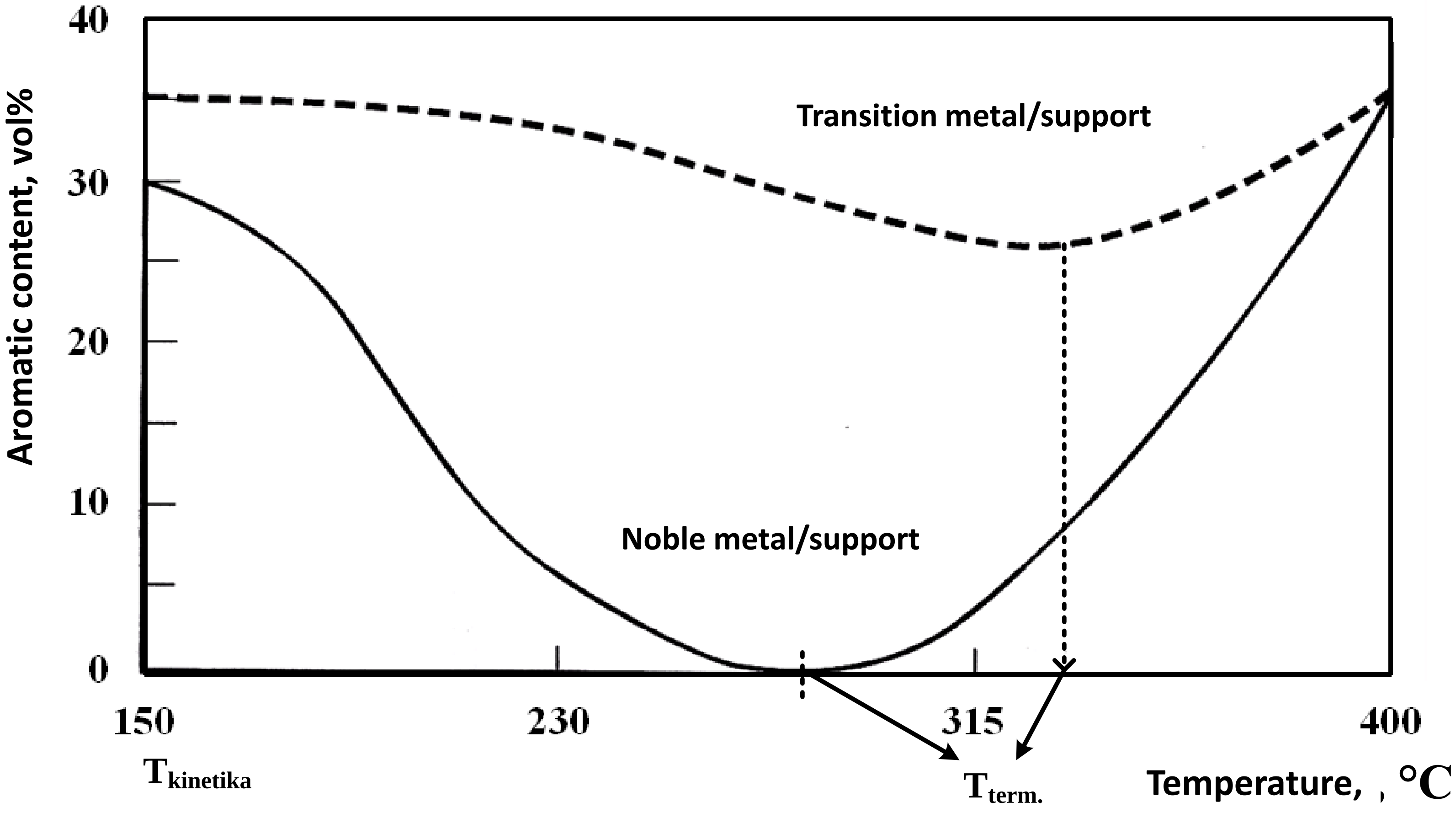


(a reakcióhő az alkillánc méretének növekedésével csökken; egyre kevésbé exoterm a reakció)

- **naftalinból dekalin: ΔH = -335 kJ/mol**



Effect of **reaction temperature** on aromatic saturation



Catalysts of aromatic hydrogenation

- **High sulphur tolerance** catalysts (feed sulphur content 250< mg/kg)
  - Mo, W (VI. group) és Co, Ni (VIII. group), in sulphide state, on γ-Al_2O_3 support

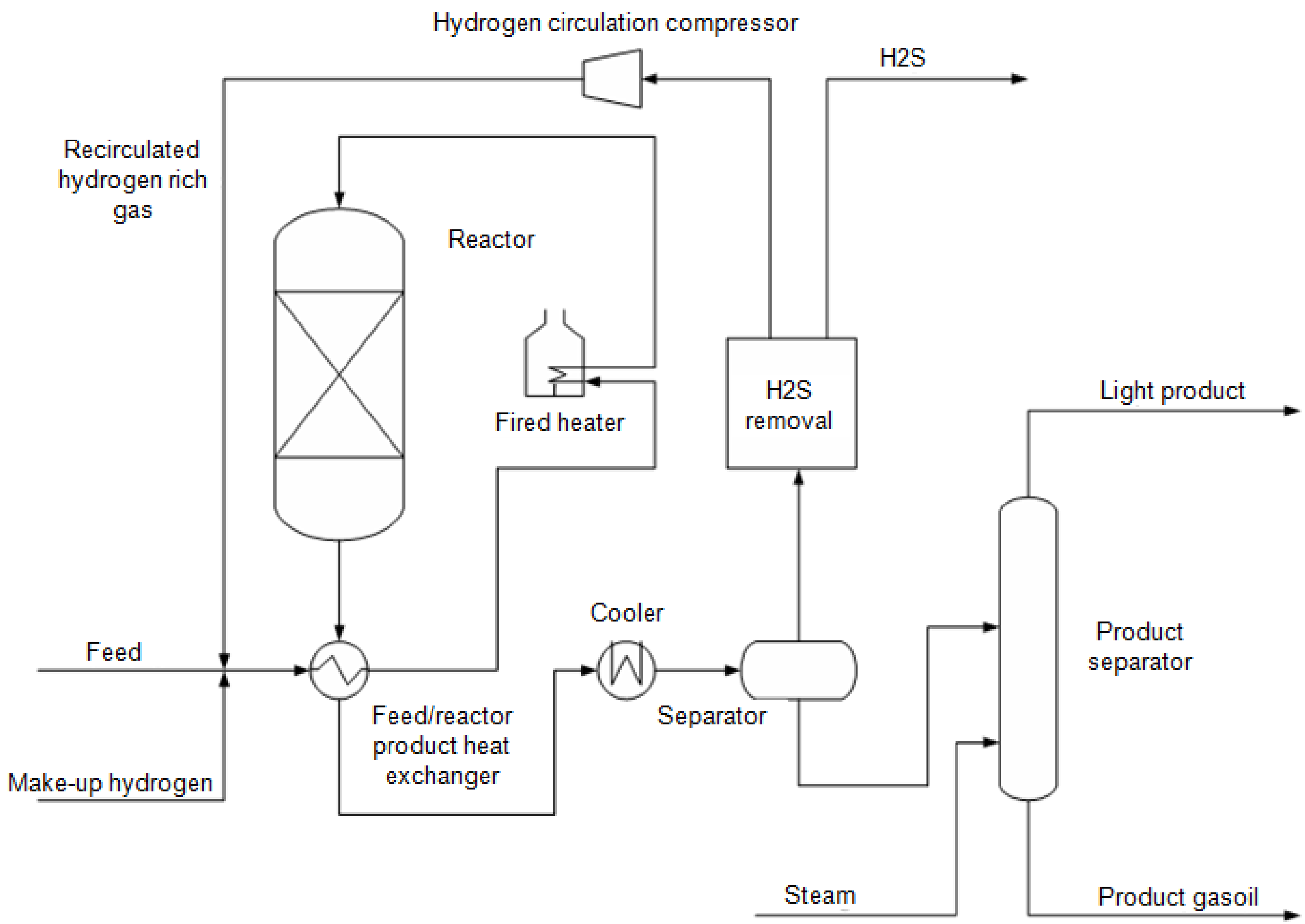
    Activity order: Mo > W >> Ni > Co
  - $NiMo/Al_2O_3$, $CoMo/Al_2O_3$, NiW/Al_2O_3 in sulphide state

    Activity order: NiW > NiMo > CoMo > CoW
  - Only partial aromatic saturation (up to max. 50-80 %; min. 60 bar H_2 partial pressure)
- **Low sulphur tolerance** catalysts (feed sulphurcontent <250 mg/kg, rather <10-20 mg/kg)
  - Pt or Pt, Pd amorphous Al_2O_3-SiO_2, or acidic (USY) support
  - High aromatic saturation (up to 95 %-ig; T_{max}: 300-310 °C, pH_2: 25-40 bar)

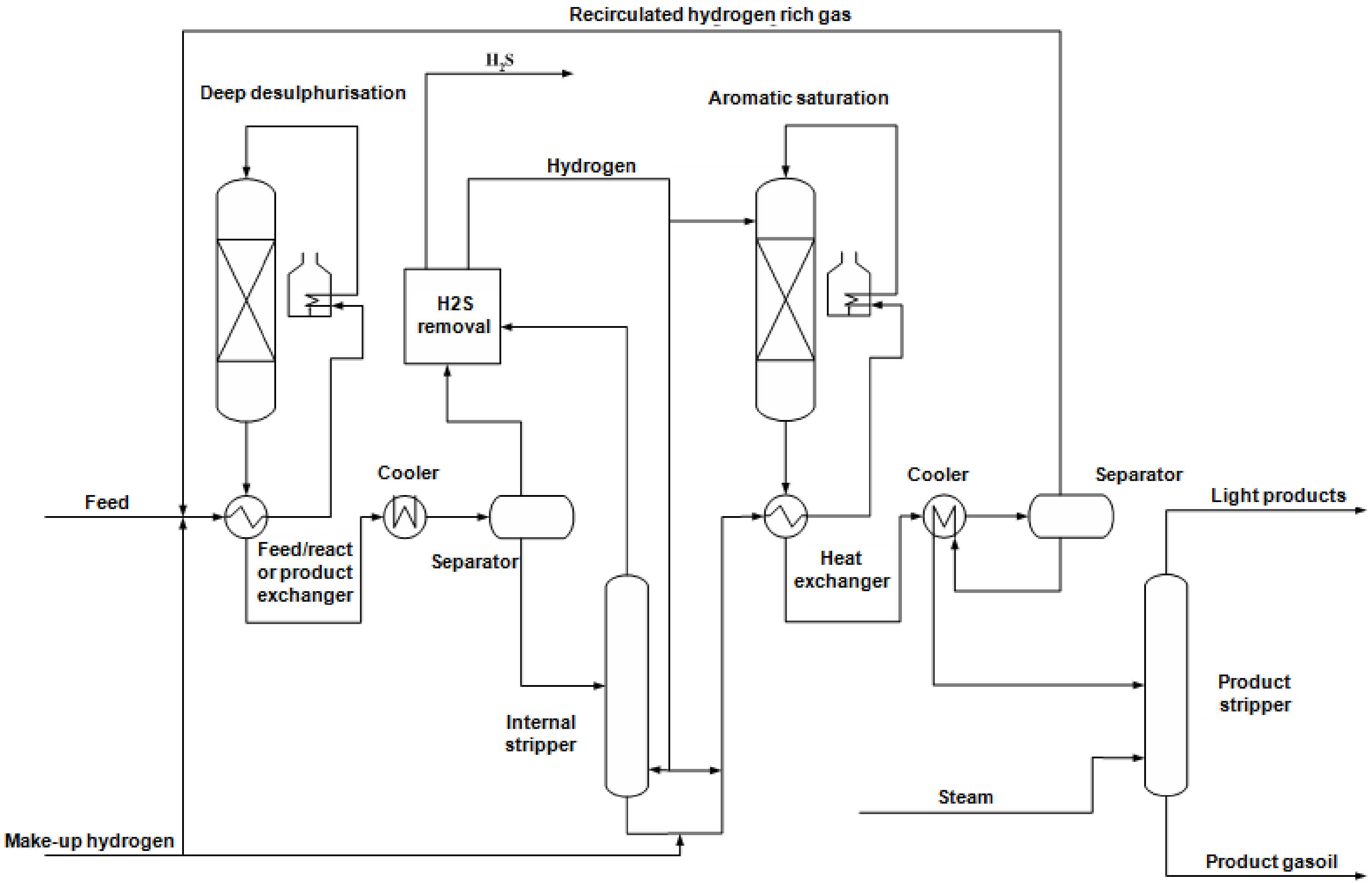
Industrial solutions

- **Differences** betweeen the different solutions
  - In the order of heteroatom removal and aromatic saturation (parallel or one after the other)
  - In the number of applied number of reactors
  - In the applied catalysts
  - In the position of the catalysts (eg. separated beds)
  - In the cooling mode
  - In the applied process parameters
- The main classification of the industrial processes
  - Single step
  - Two step processes

Single step technology

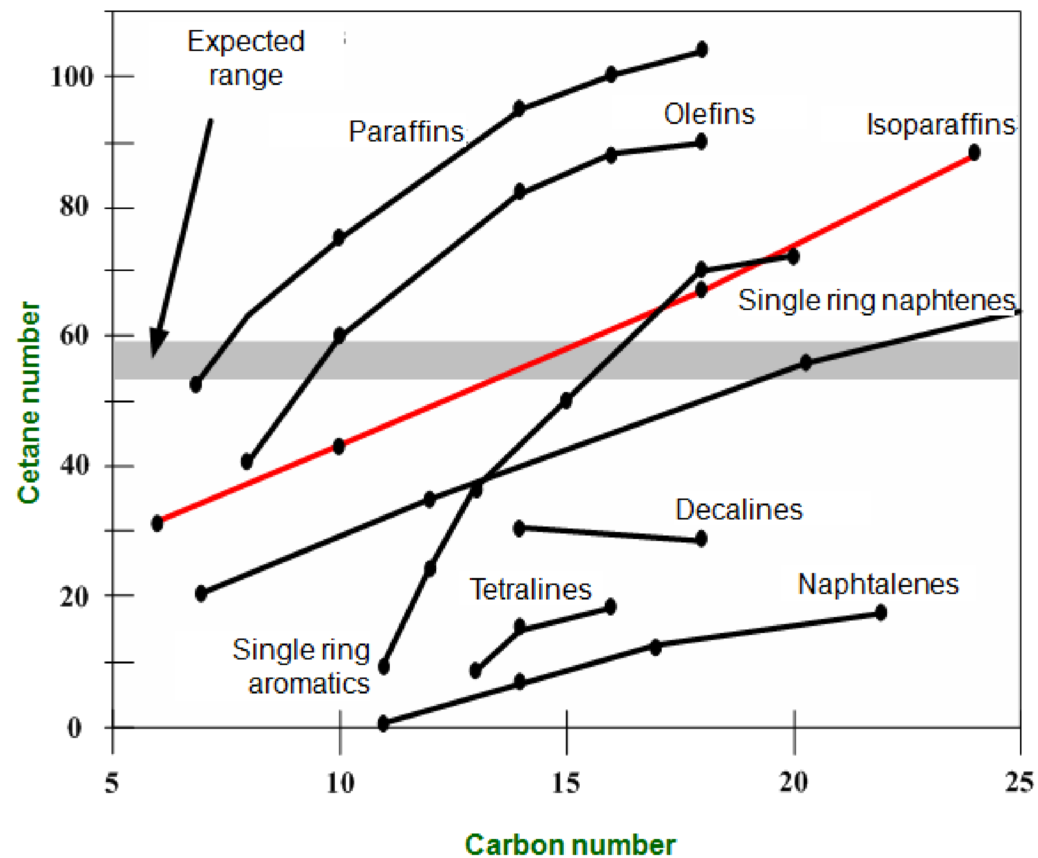


Two step technology

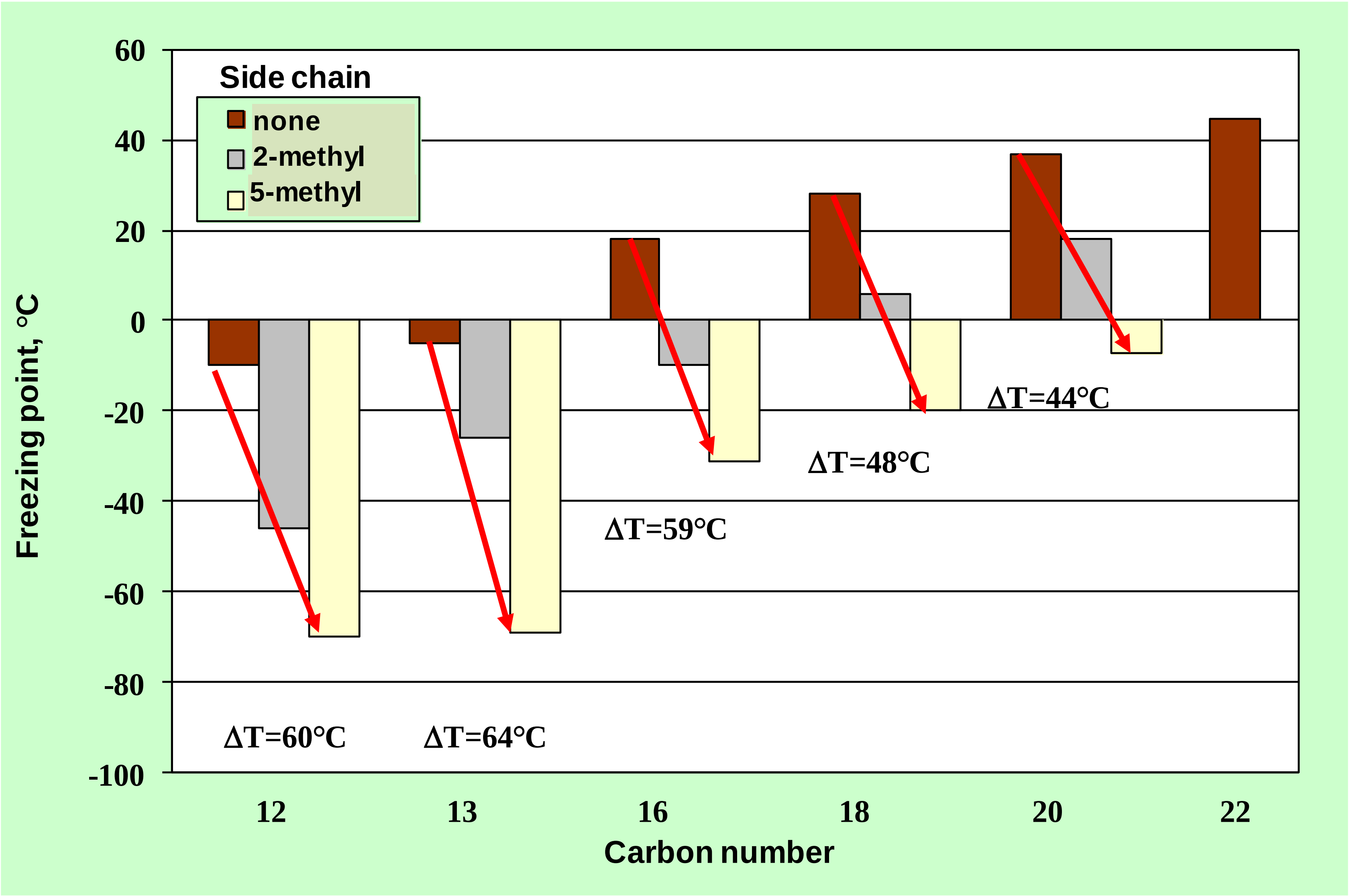


B. Conversion of **paraffin content** of gasolines

- Goal of paraffin conversion
  - Freezing point os n-paraffins are high – at low temperature they cristallize and plug the fuel lines
- Freezing point decrease options:
  - Selective hydrocracking
  - Selective izomerisation
  - Combination ot aboves
- Measurement:
  - Cold filter pluggig point (CFPP)



Effect of **izomerisation** on freezing point



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The End