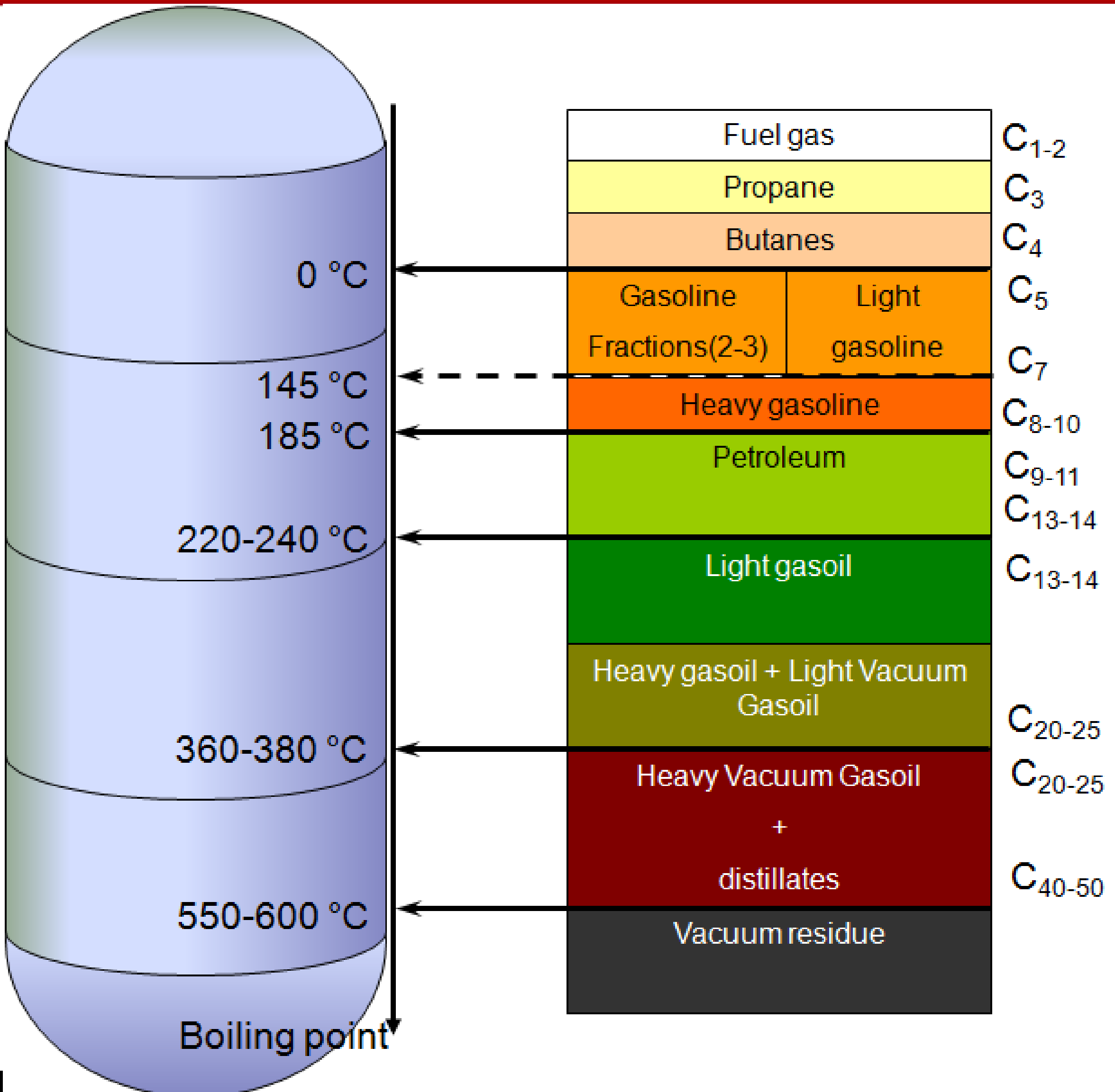
Hydrocarbon processing
Conversion processes

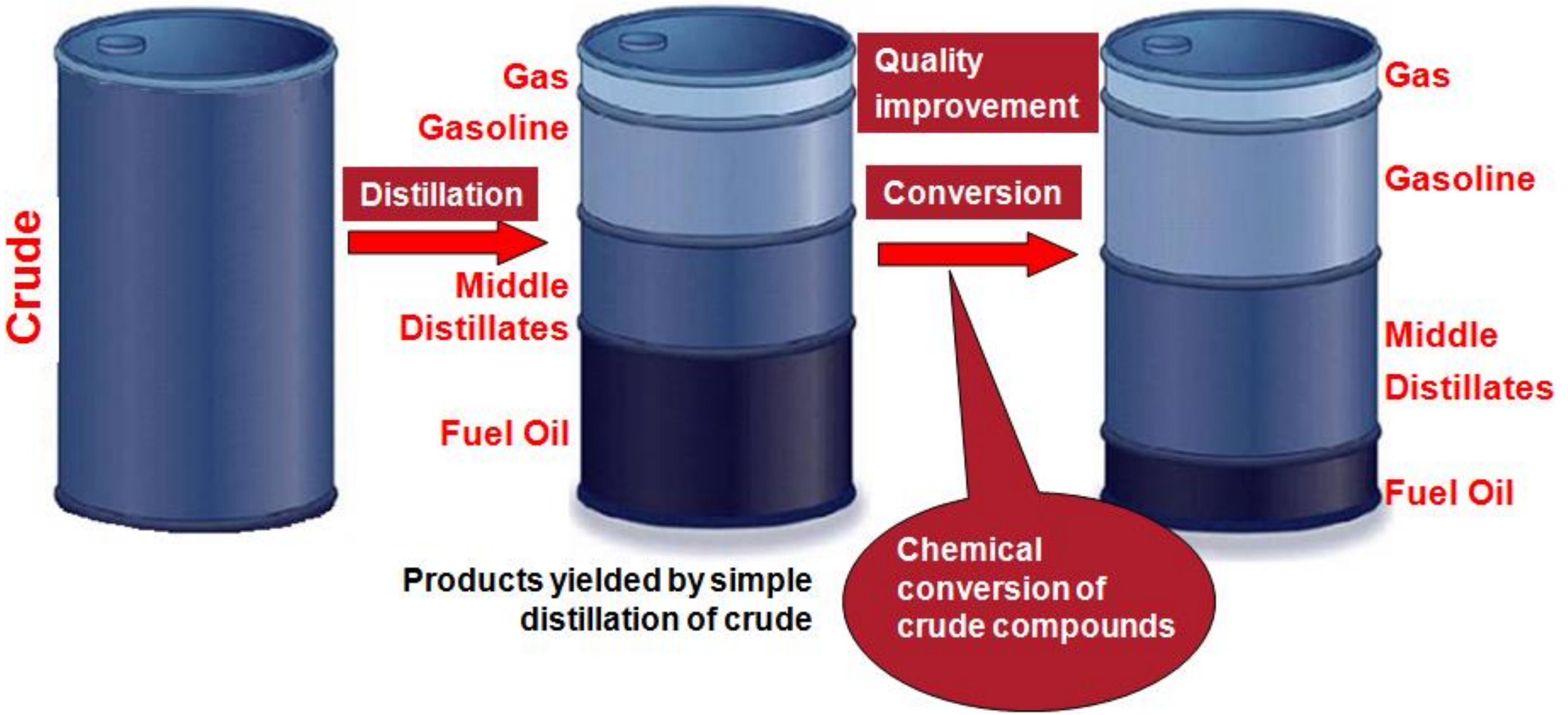
English version based on the presentation of
Szalmásné Dr. Pécsvári Gabriella held in 2014

Fractions of crude oil



Goal of Refining

Main goal: economic production of product structure according to market demand



The whole process is called „refining".

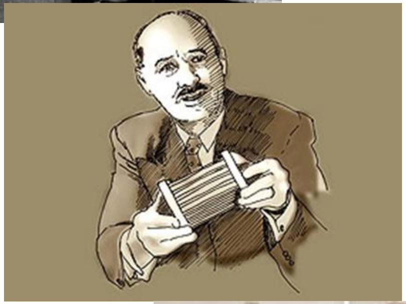
Conversion processes

Driving force:

- Product slate according to market demand (quantity demands/flexibility)
- More valuable product from one unit crude oil (economicity)

Cracking

1910, Burton, thermal cracking
Gasoline from crude oil

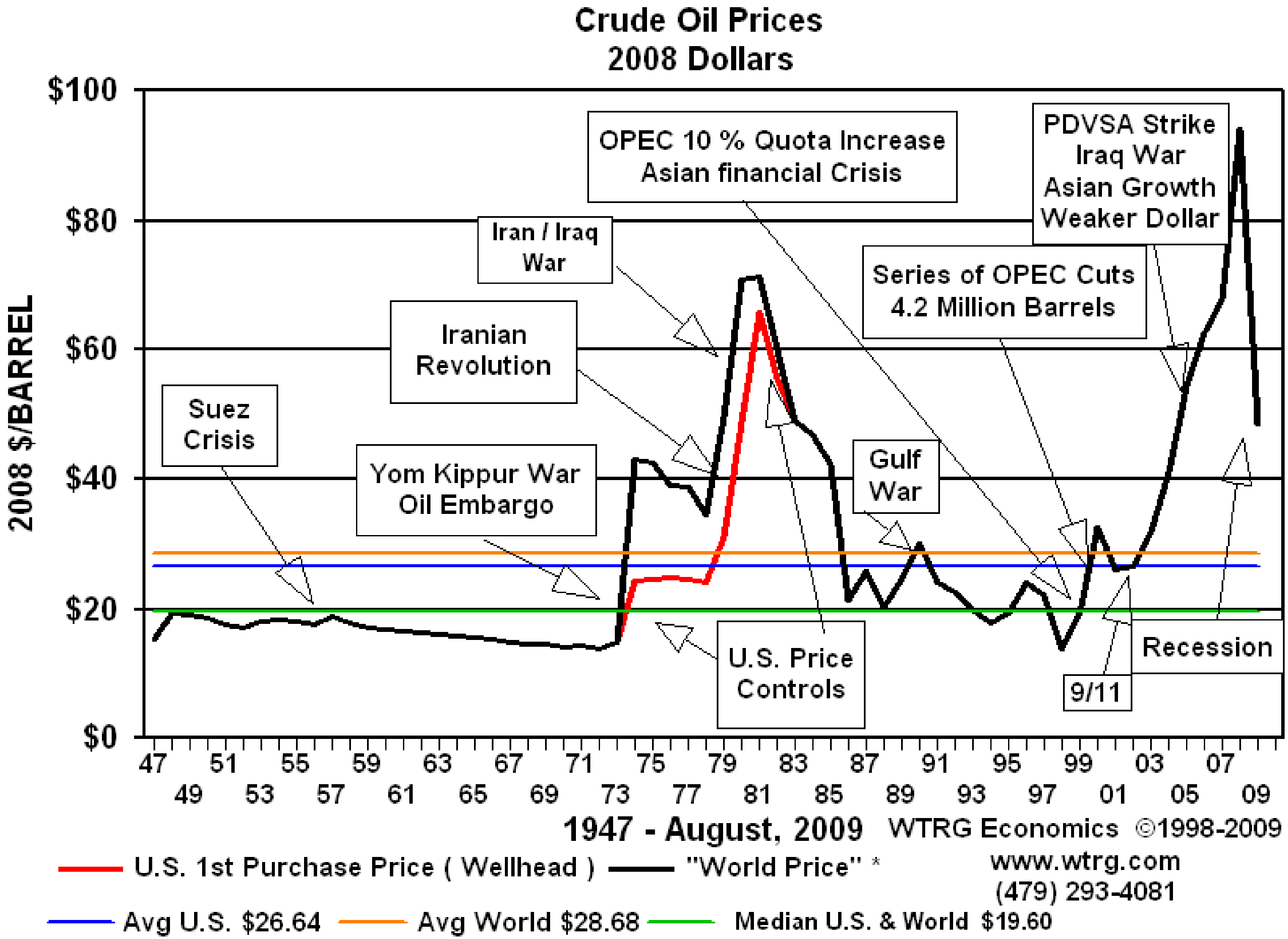


1920, Eugene Jules Houdry
Catalytic process: gasoline from lignite

1936
First catalytic cracking unit in New Jersey

1942
First fluid catalytic cracking unit

Crude oil price and high politics



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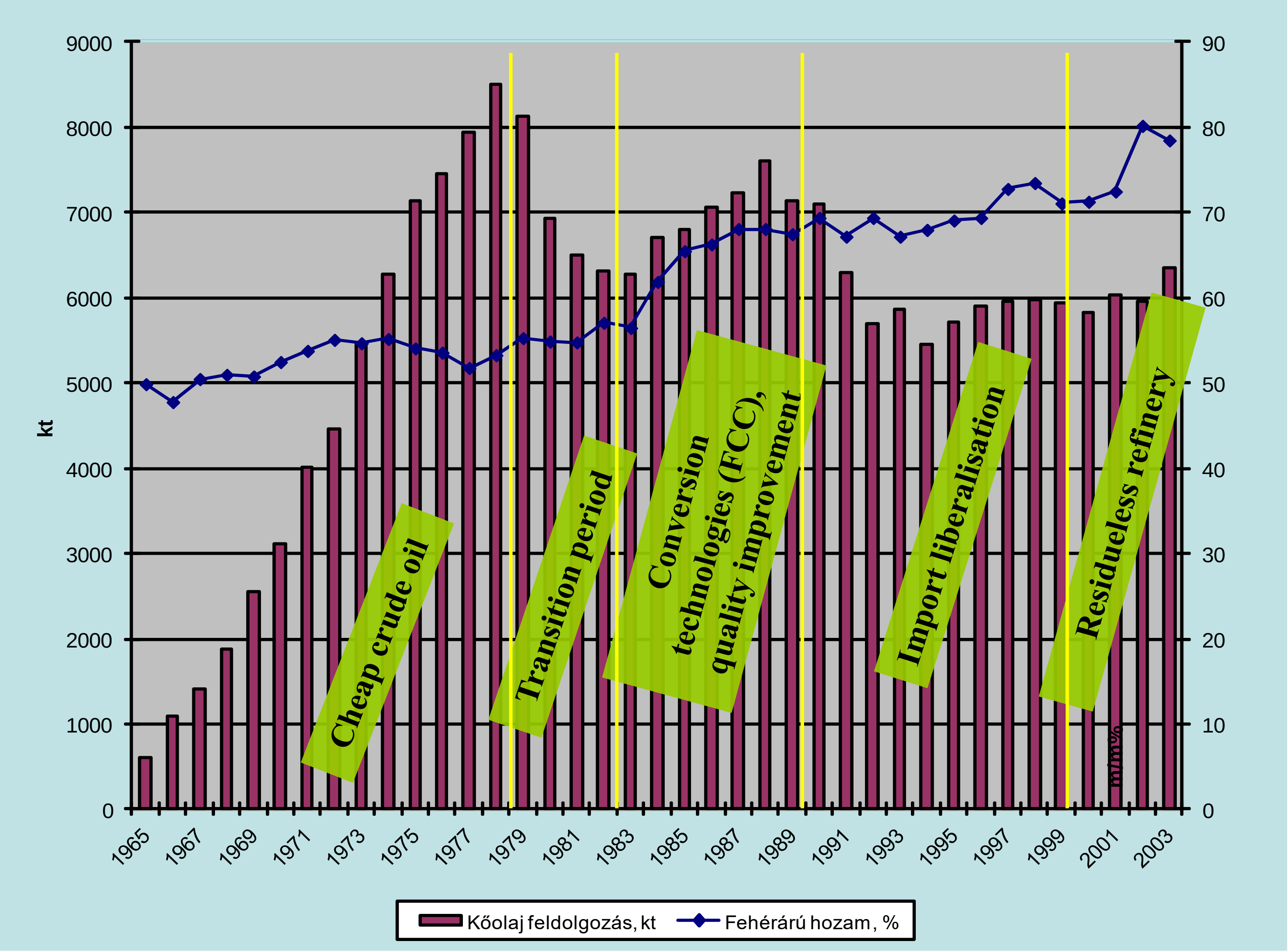
DR: crude oil processing and white product yield



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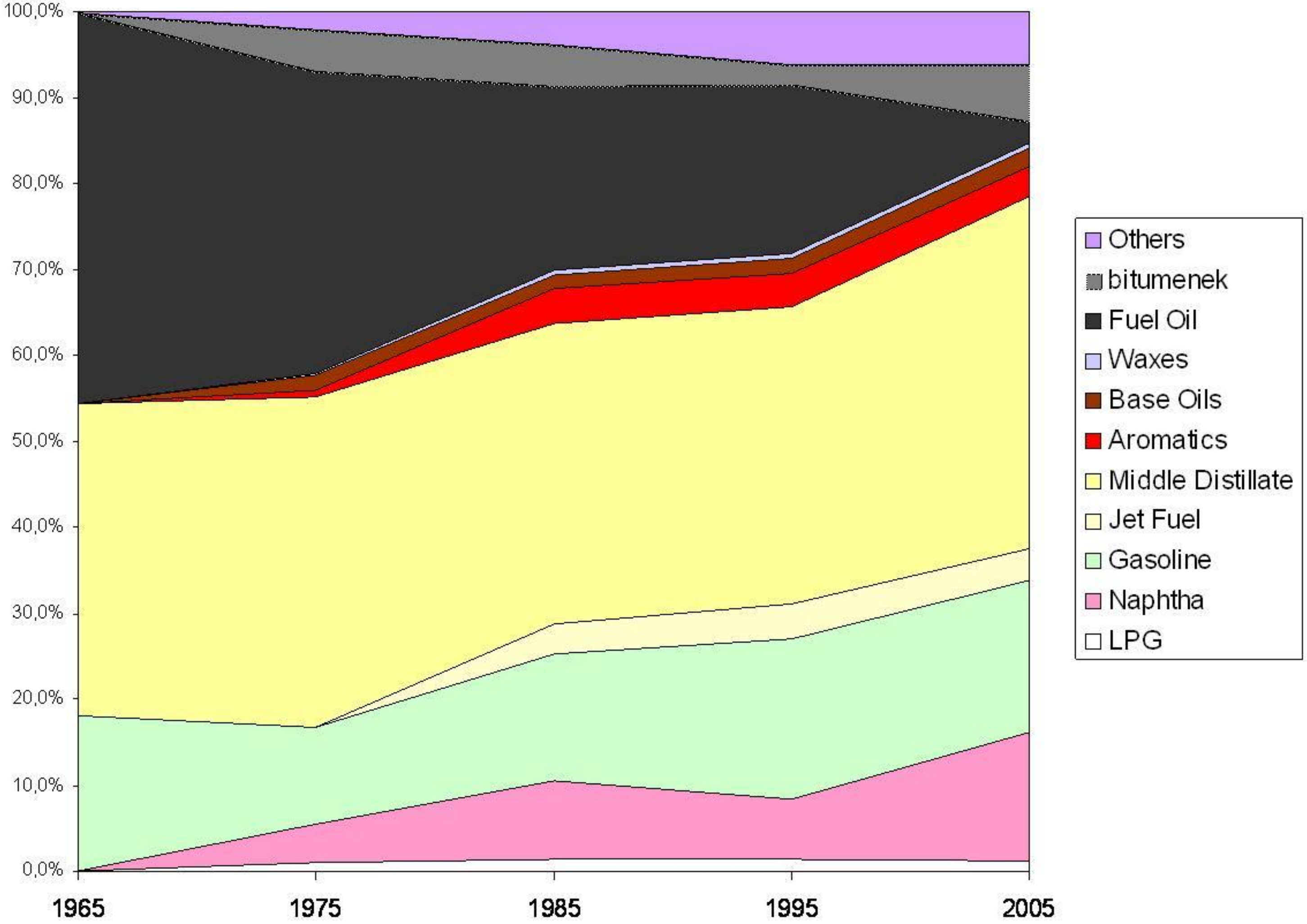
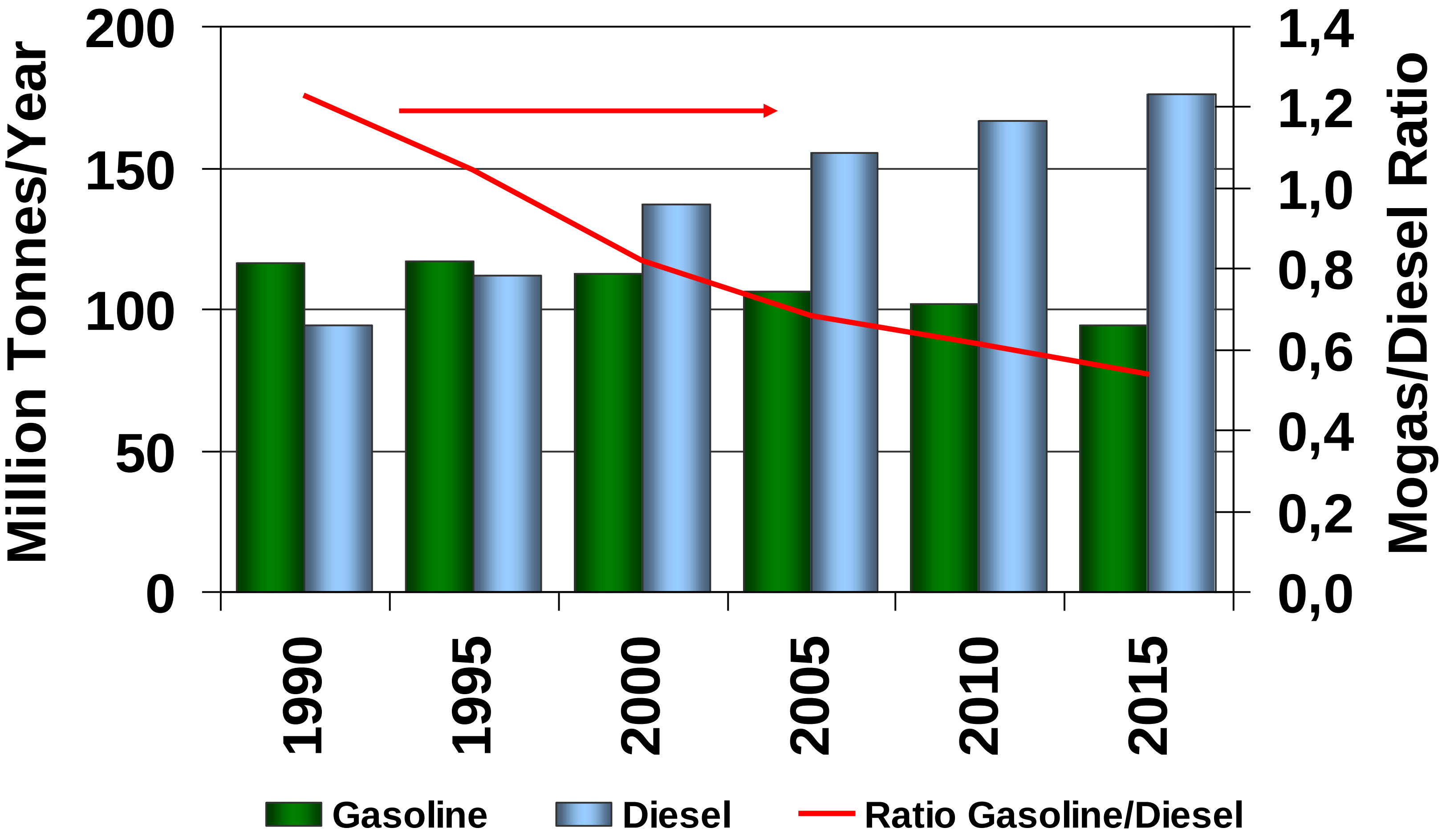
Flexibility of refineries

Alteration of DR product slate in the past



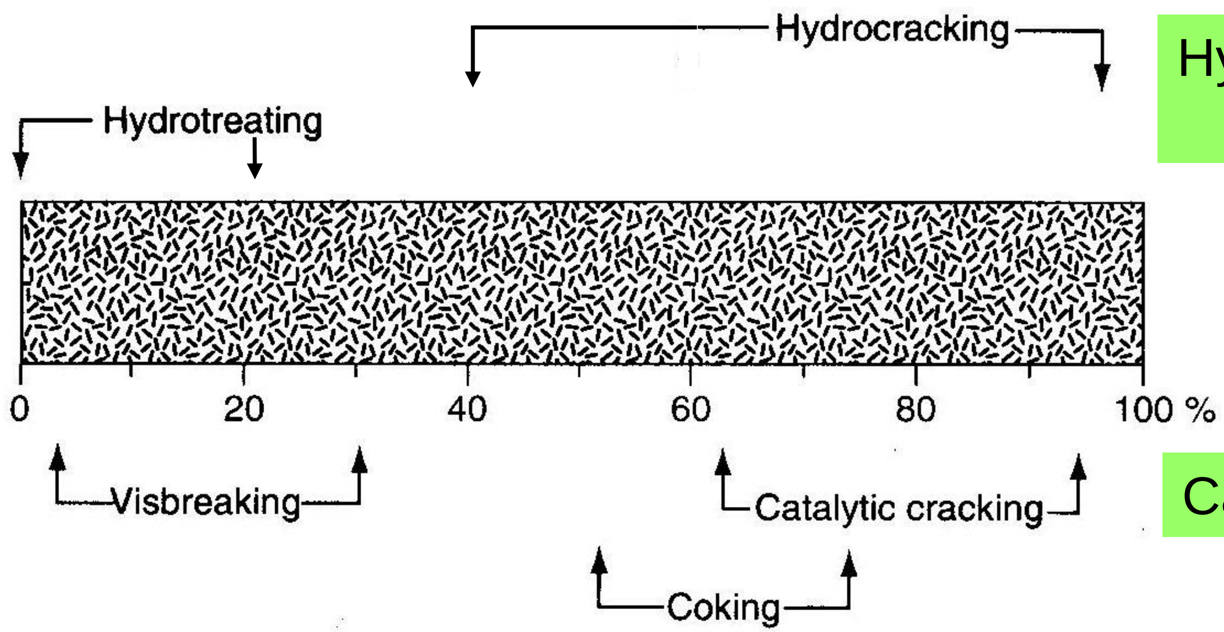
EU 15 gasoline and diesel demand



Source: History IEA; Forecast Purvin & Gertz

Conversion processes

Feedstock conversion of different processes:



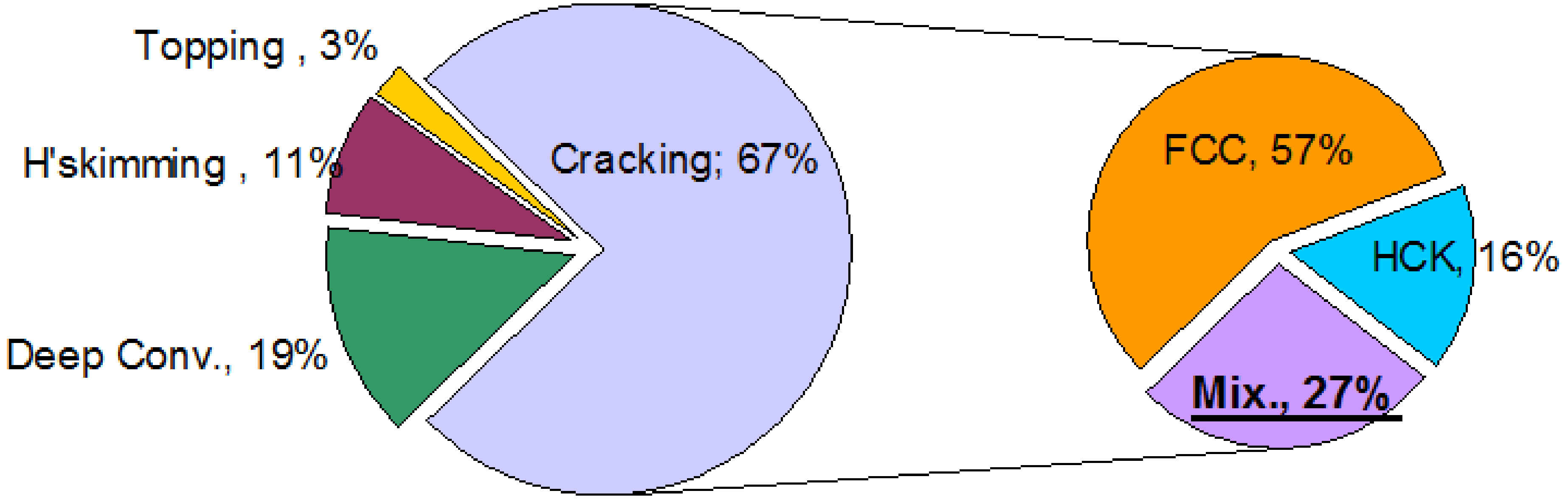
Hydrogen introduction

Carbon removal

According to feedstock:
vacuum distillate
vacuum residue

Thermal/Catalytic

Cracking processes in the EU refineries



Conversion processes – Catalytic cracking

Goal: cracking of vacuum distillates molecular weight and boiling point reduction

Feed: vacuum distillates

Products: C_3-C_4 mixture, FCC gasoline, gasoil (LCO)

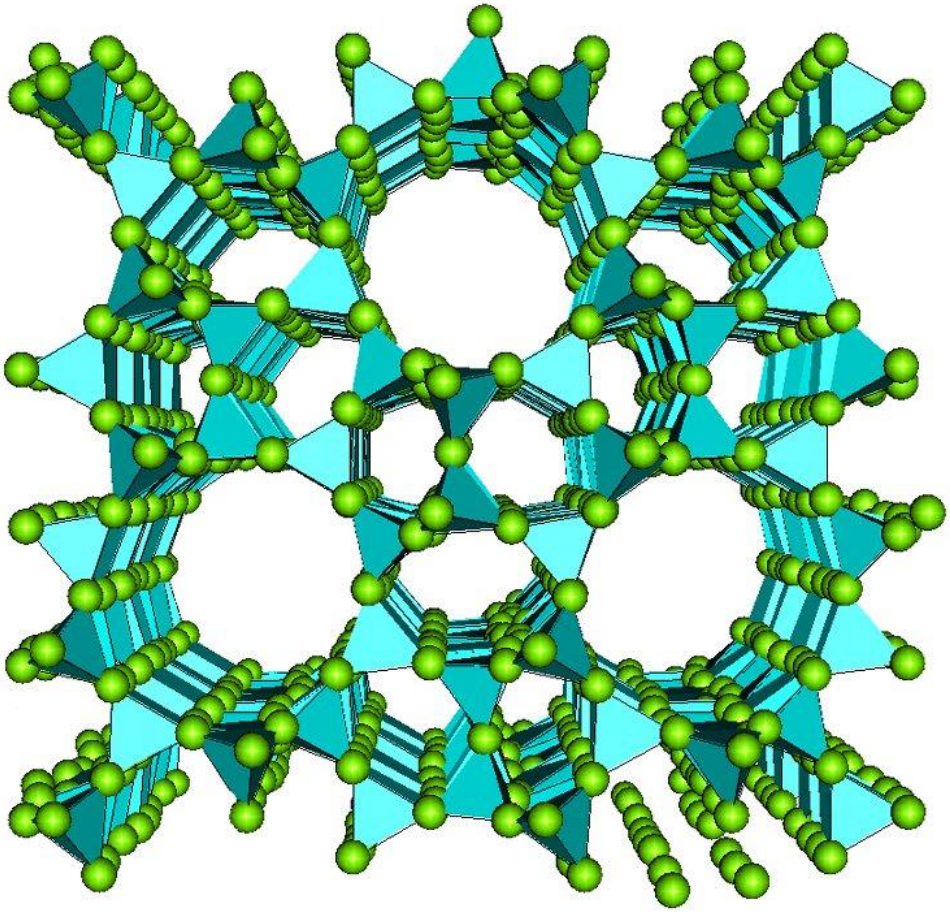
Process parameters:

Temperature: 520 - 540 °C

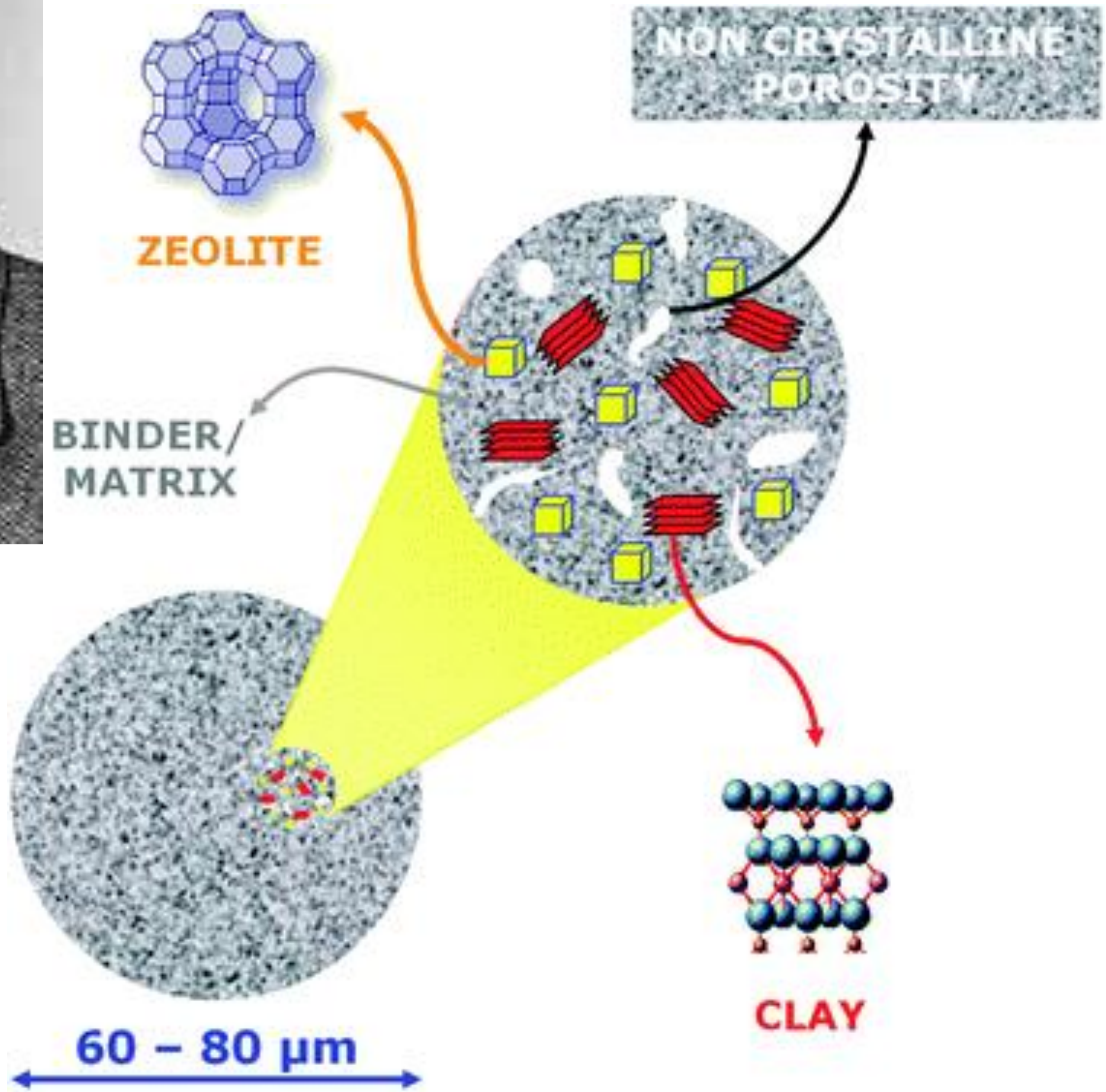
Pressure: 2 – 4 barg

Contact time: 1-2 seconds

Catalyst: zeolites (Al_2O_3 - SiO_2)



Rabó Gyula
1924-2016



Catalytic cracking – Reactions

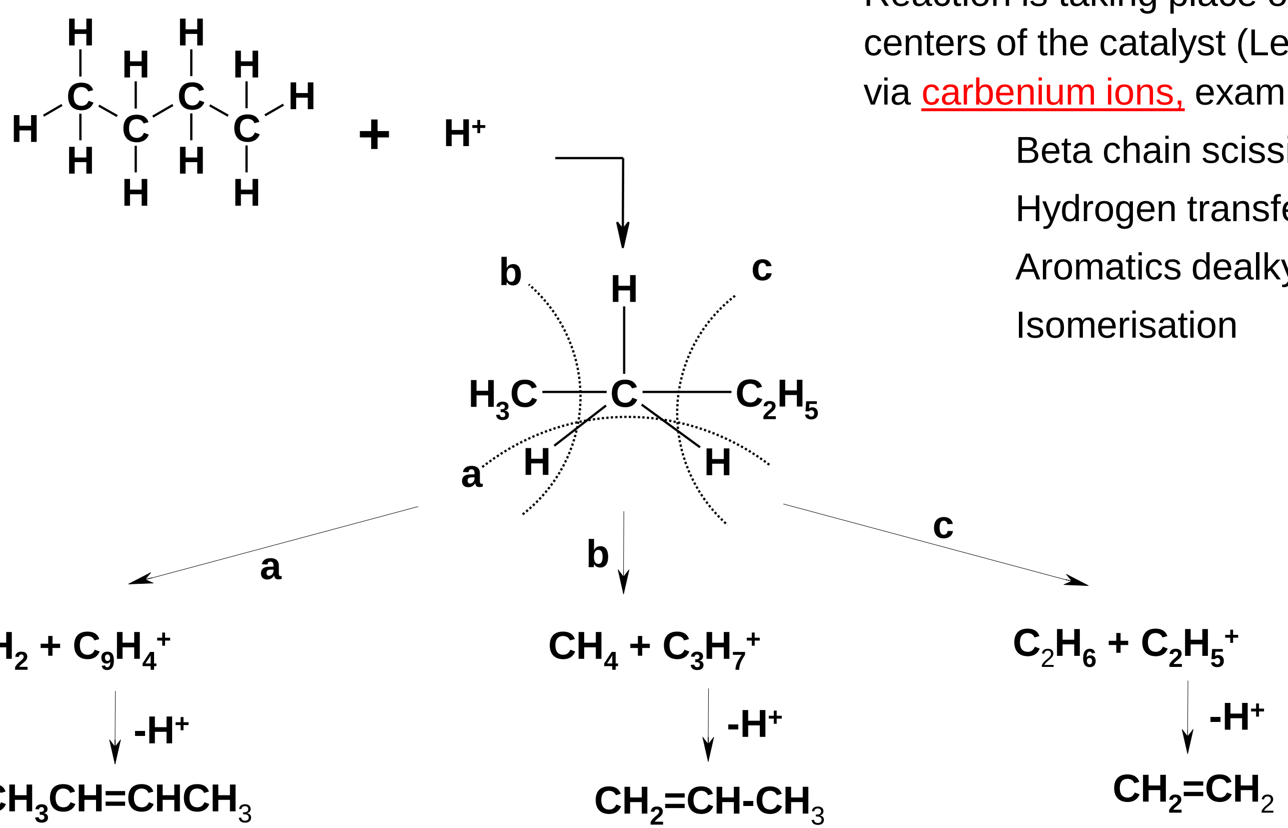
Cracking reactions:

Thermal cracking
Catalytic cracking
Dehydrogenation
Hydrogen transfer
Polimerisation

- **Yield**
- **Component structure**
  (olefin, aromatic)
- **Quality**
  (RON, Cetane number)

Fluid Catalytic Cracking – FCC

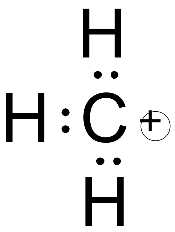
Main reactions:



Starting reaction is the carbenium ion formation

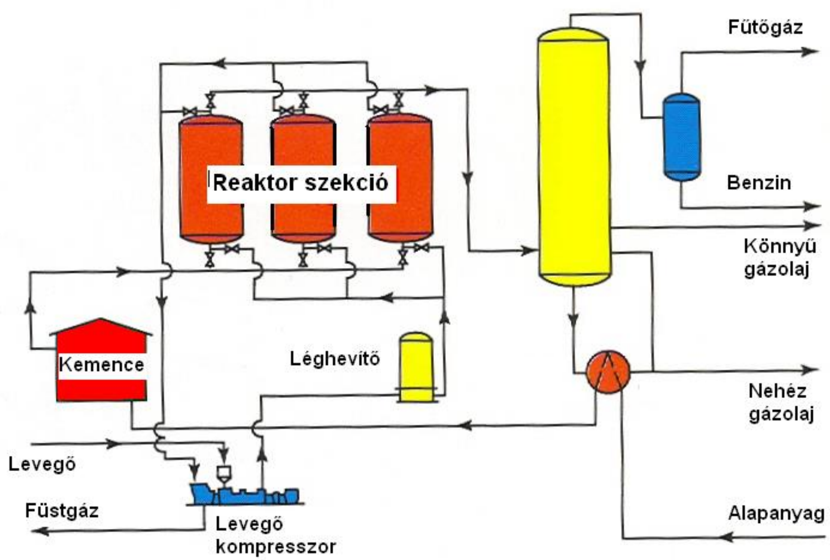
Reaction is taking place on the acidic centers of the catalyst (Lewis/Bronsted) via carbenium ions, examples:

- Beta chain scission
- Hydrogen transfer
- Aromatics dealkylation
- Isomerisation

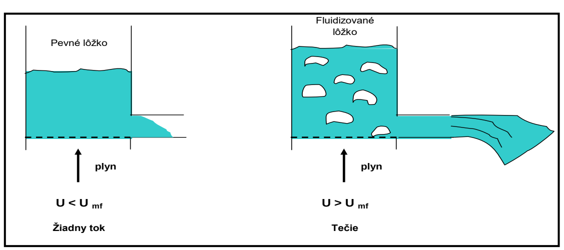


Fluid Catalytic Cracking

Houdry fixed bed cracking

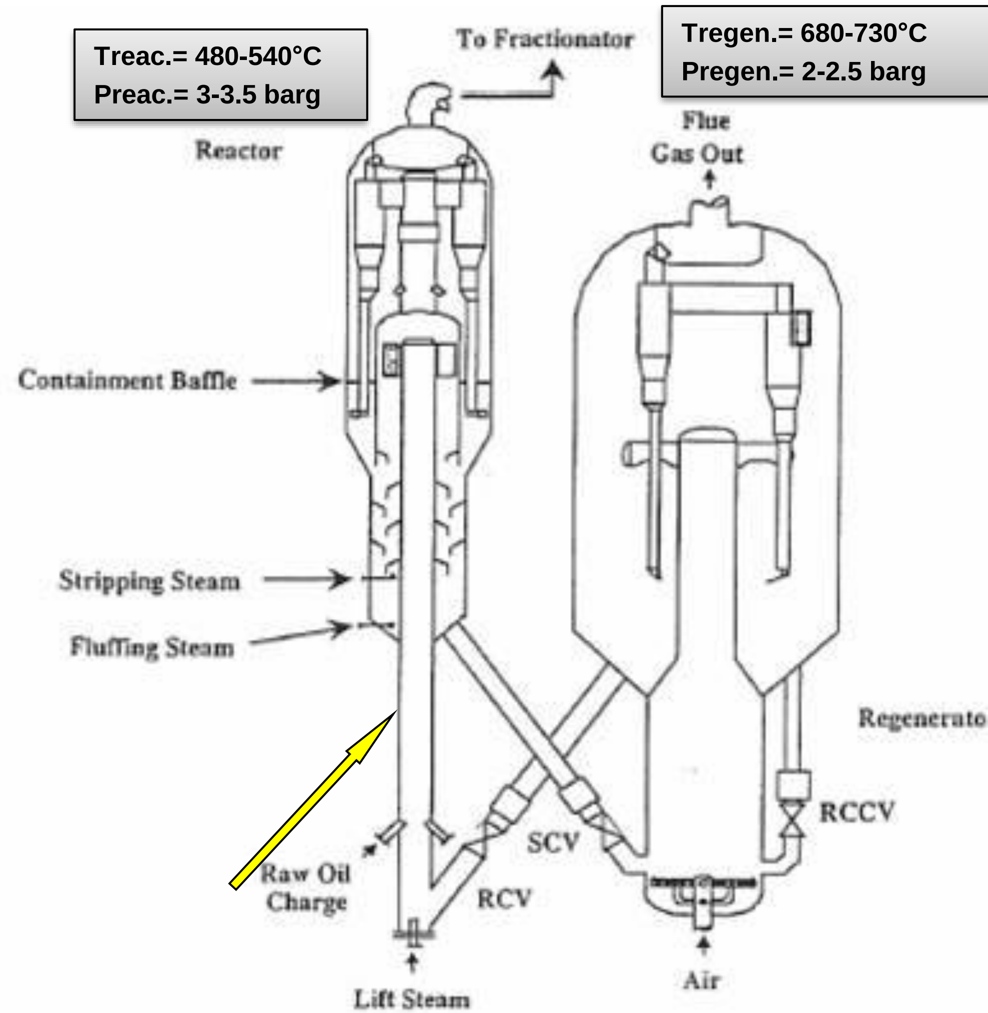


Fluid bed – continuous catalyst activity



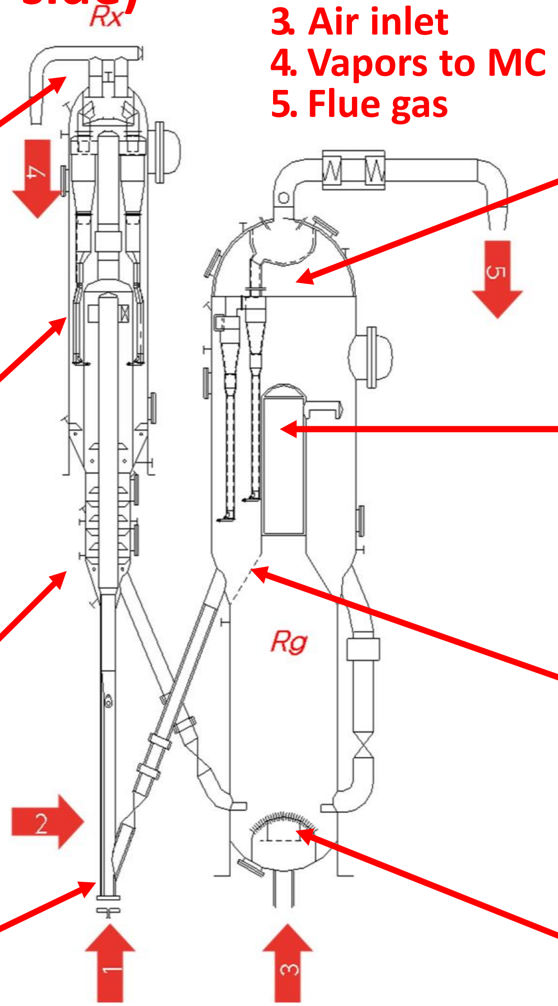
Fluid bed

Reaction is taking place in the „riser”



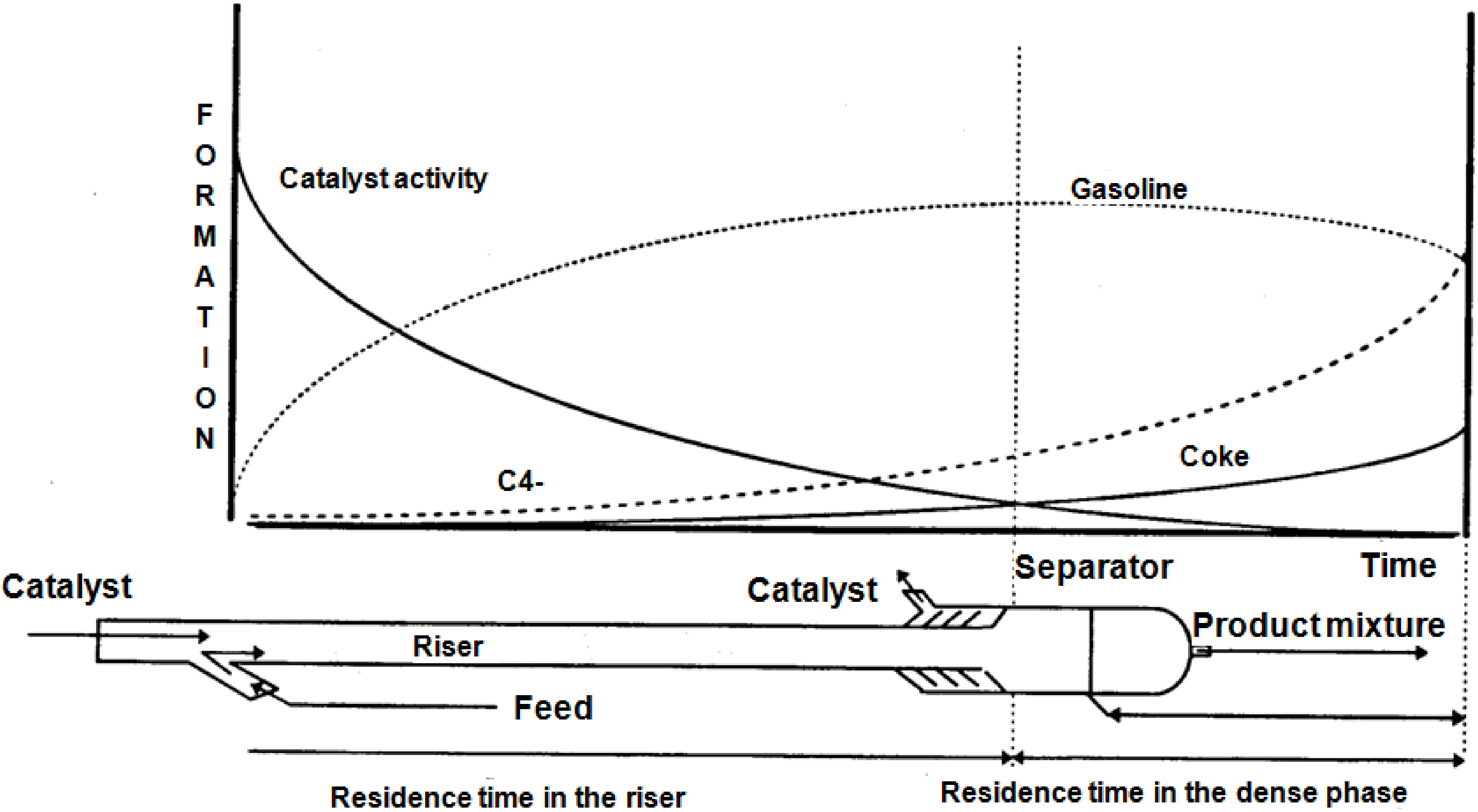
Process (UOP side by side)

1 Steam inlet
2. Feed inlet
3. Air inlet
4. Vapors to MC
5. Flue gas



• KONVERZIÓS TECHNOLÓGIÁK / FCC - CIKLONOK

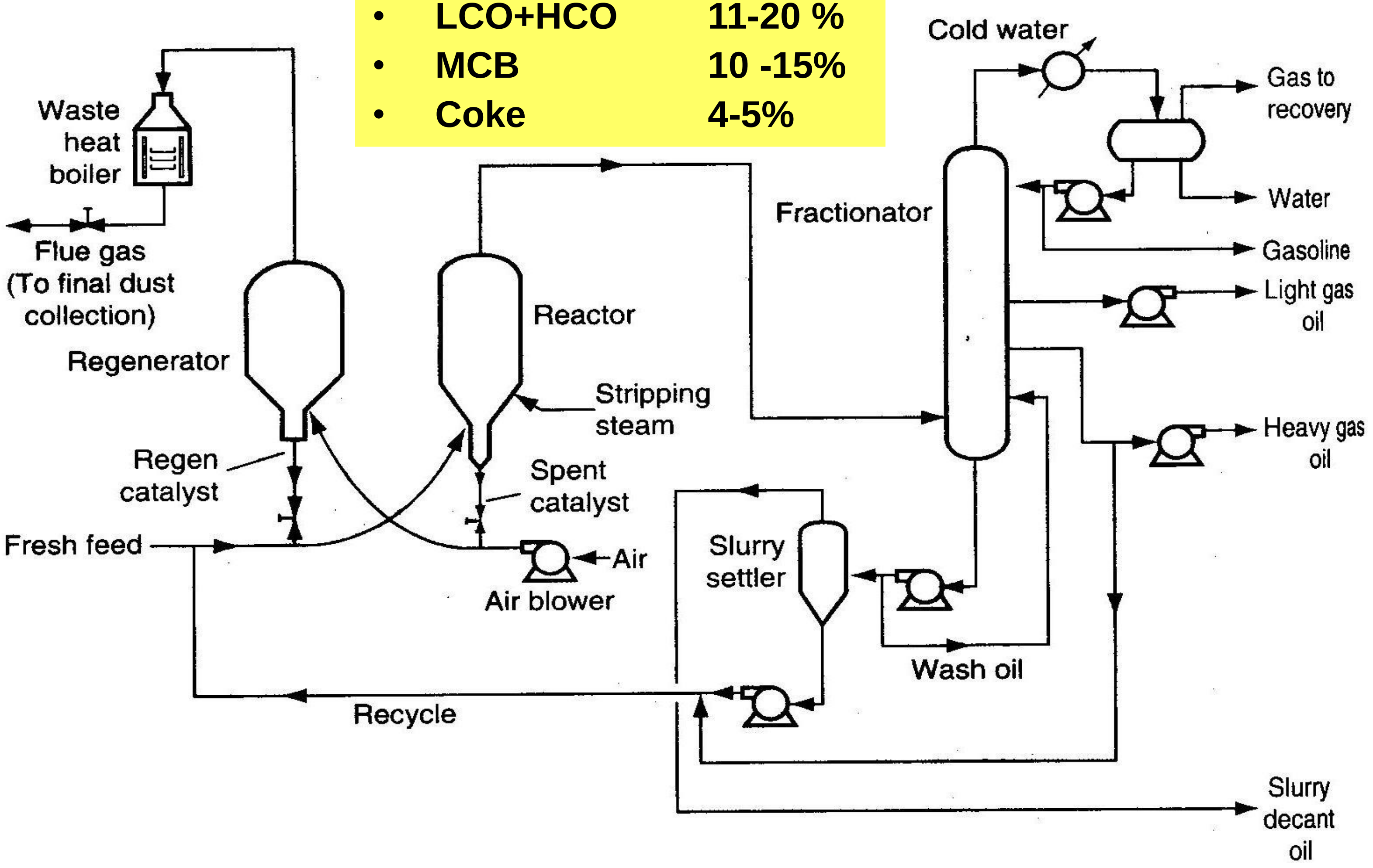
Fluid Catalytic Cracking



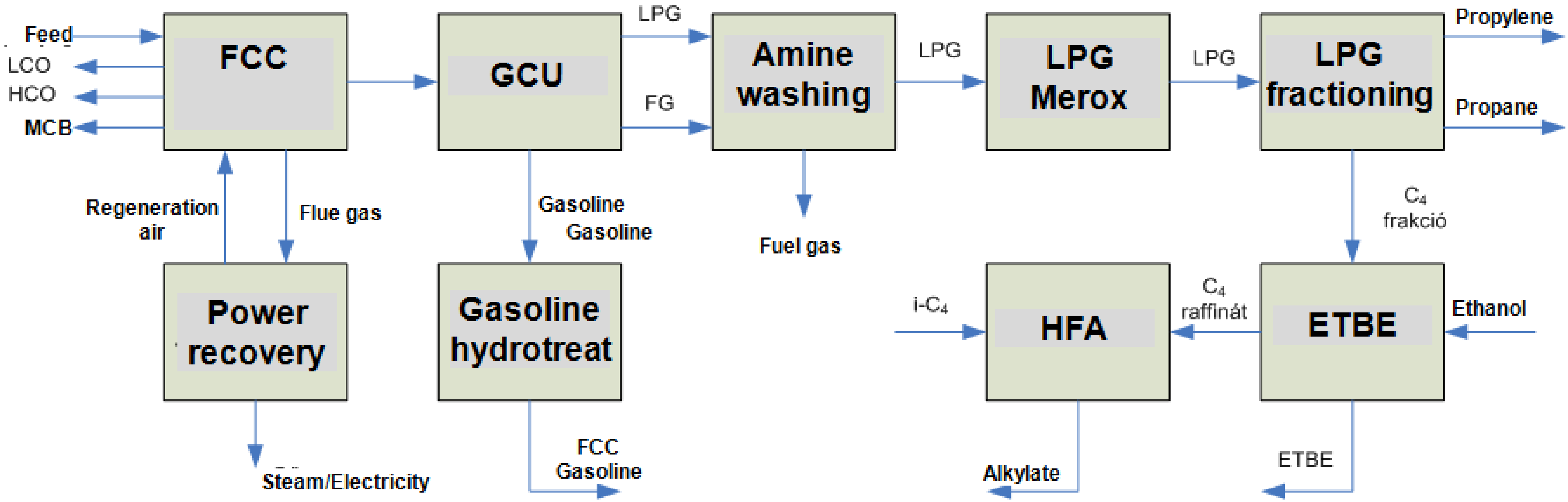
Fluid Catalytic Cracking

Product distribution:

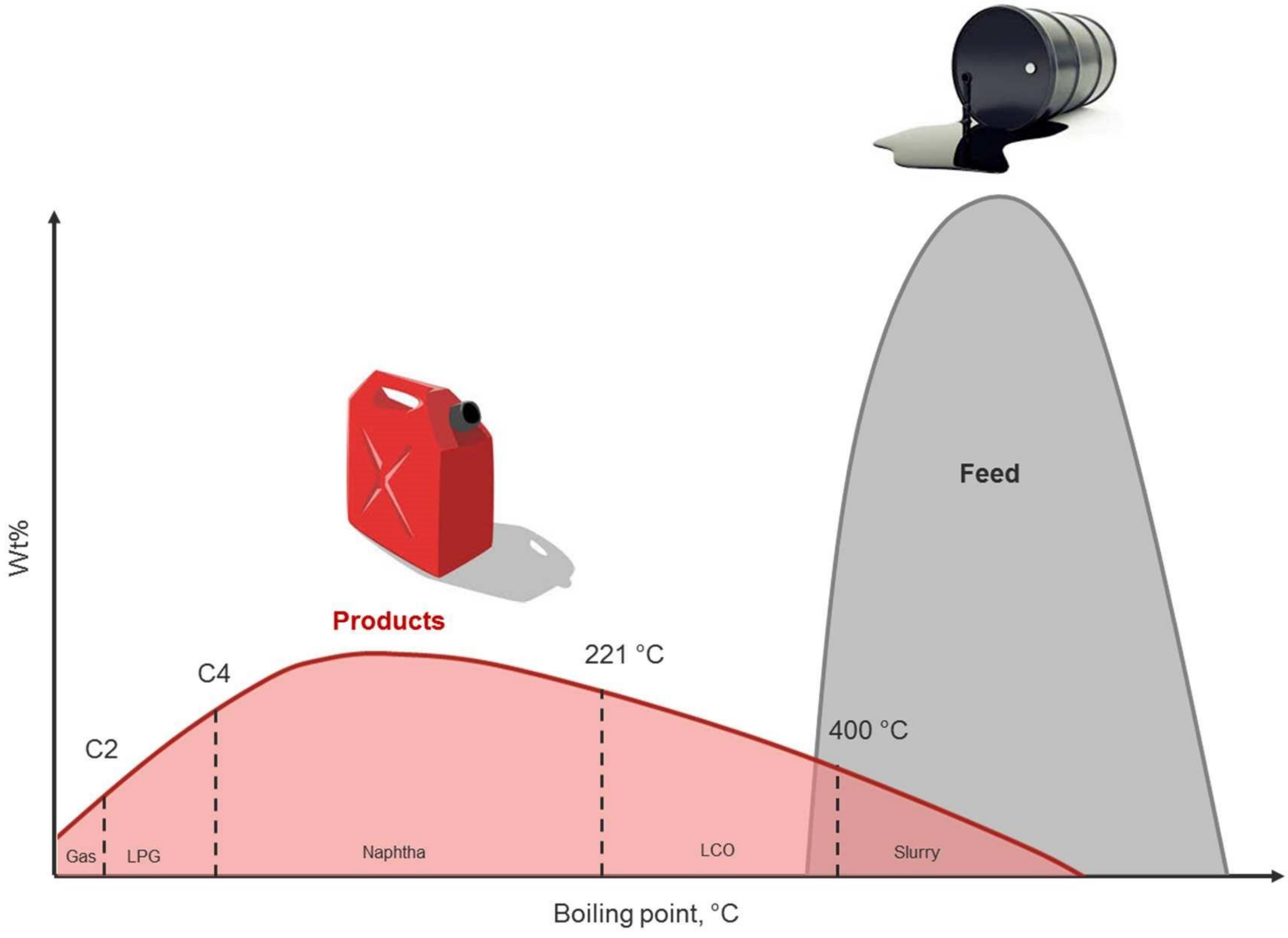
• Fuel gas	3-5 %
• C3-C4 fraction	7-20 %
• Gasoline	30-60 %
• LCO+HCO	11-20 %
• MCB	10 -15%
• Coke	4-5%



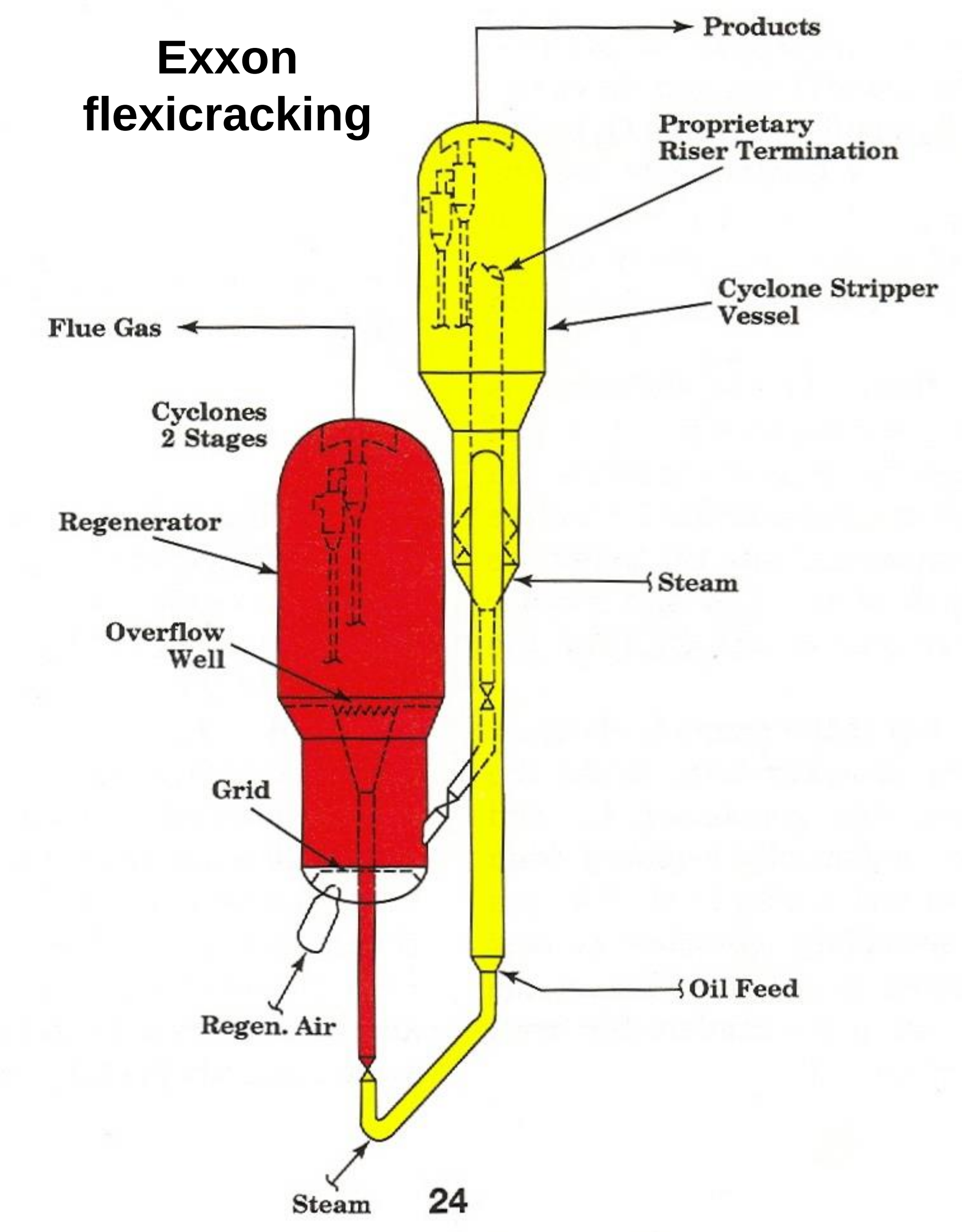
Fluid Catalytic Cracking – FCC complex block scheme

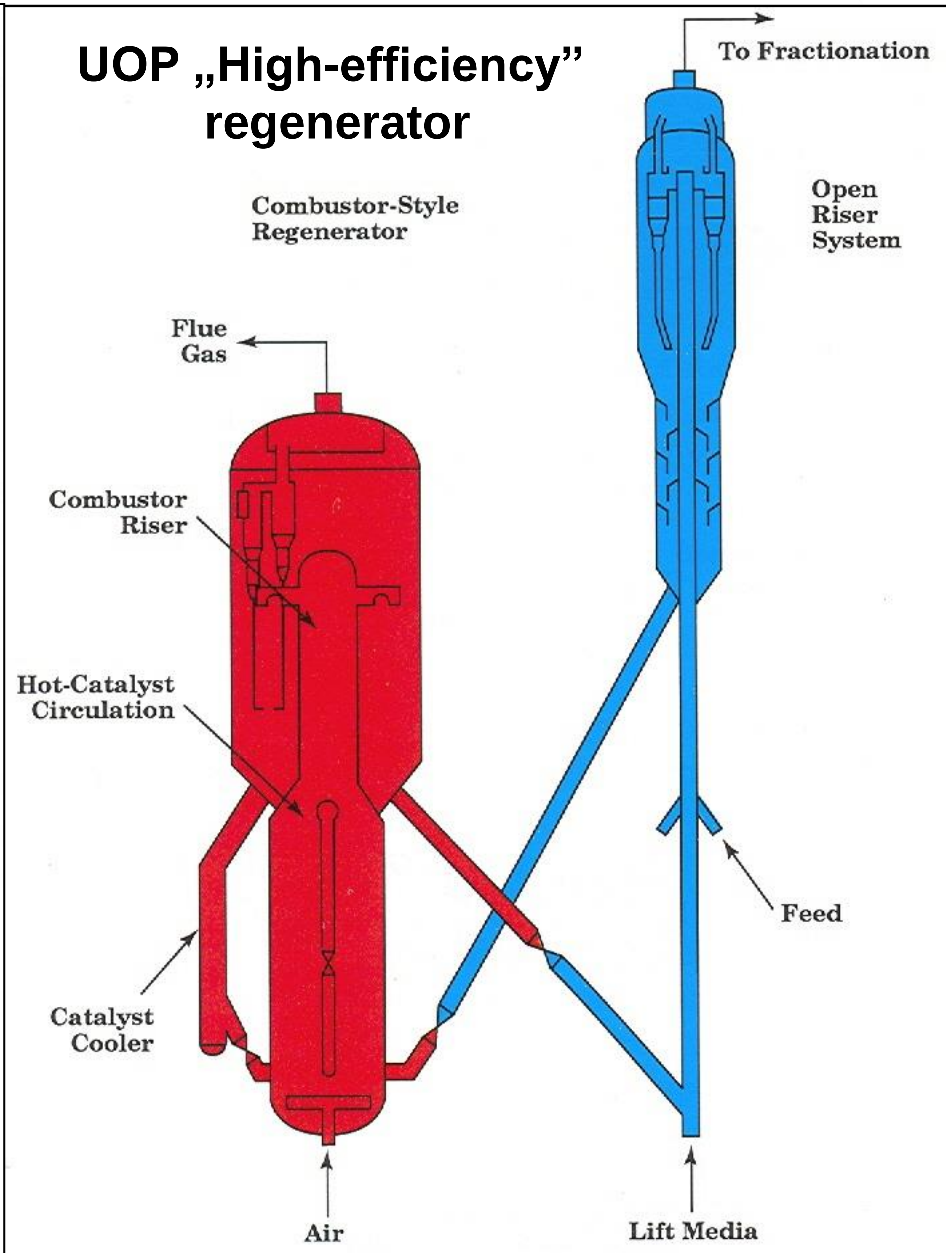


• TIPIKUS TERMÉKMINŐSÉGEK



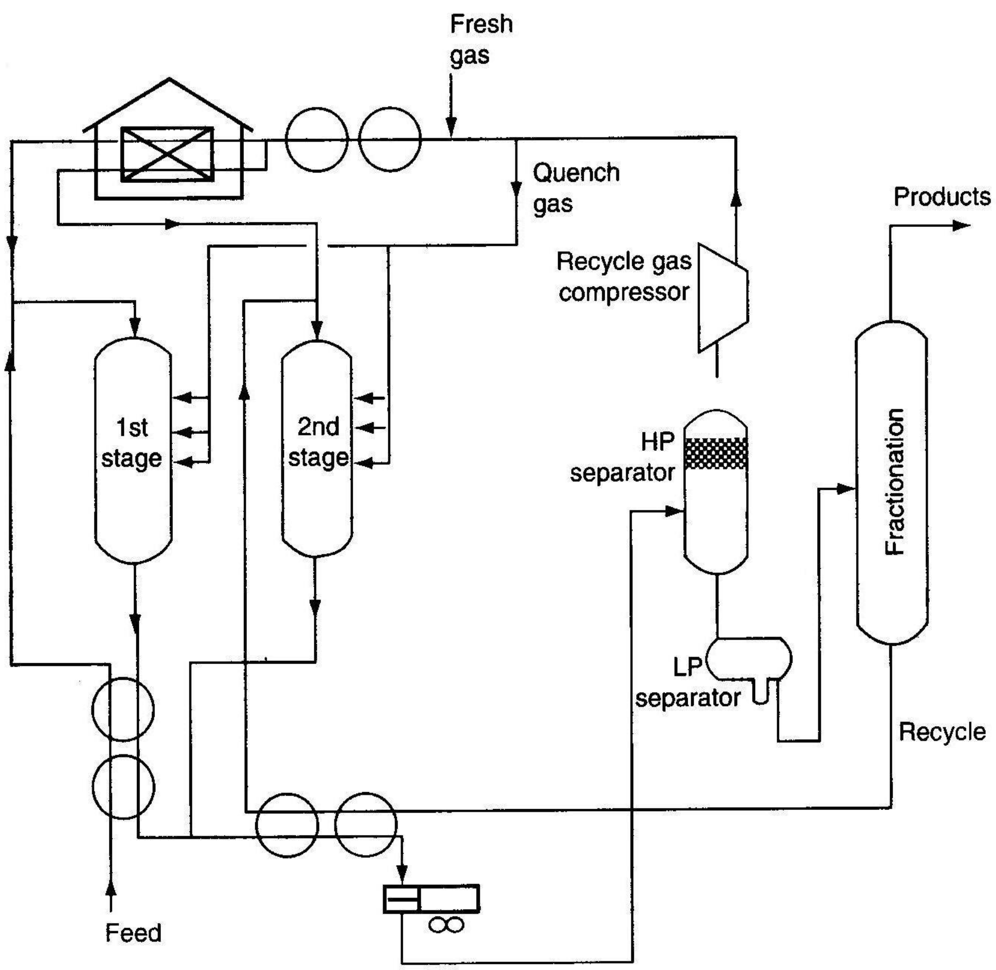
Fluid Catalytic Cracking





View of DR FCC unit

Conversion processes – Hydrocracking



Goal: Increasing the white product yield (production of smaller molecules from the feed molecules, under hydrogen atmosphere)

Feed: vacuum distillate, vacuum residue

Main products: diesel, gasoline

Process parameters:

Temperature: 300 - 450 °C

Pressure: 70 – 250 bar

Catalyst: Co/Mo/Pd/Pt on SiO_2/Al_2O_3

HDT and HCK catalysts

HCK catalysts

Acidic matrix
(cracking function)

- **amorphous** SiO_2-Al_2O_3, Al_2O_3, x-Al_2O_3 (x=halogen)
- **Low zeolite ratio - amorph** (modif.Y/ SiO_2.Al_2O_3)
- **High zeolite ratio** (modif.Y+ Al_2O_3)

Dispersed metals
(hydrotreating function)

- **Noble metals** (Pt, Pd)
- **M_XS_Y** z VIA gr. (Mo, W) + VIIIA gr. (Co, Ni)

In order to have efficient coproduction of the two function, high active surface is needed

HDT and HCK reactions

(in the order of occurence)

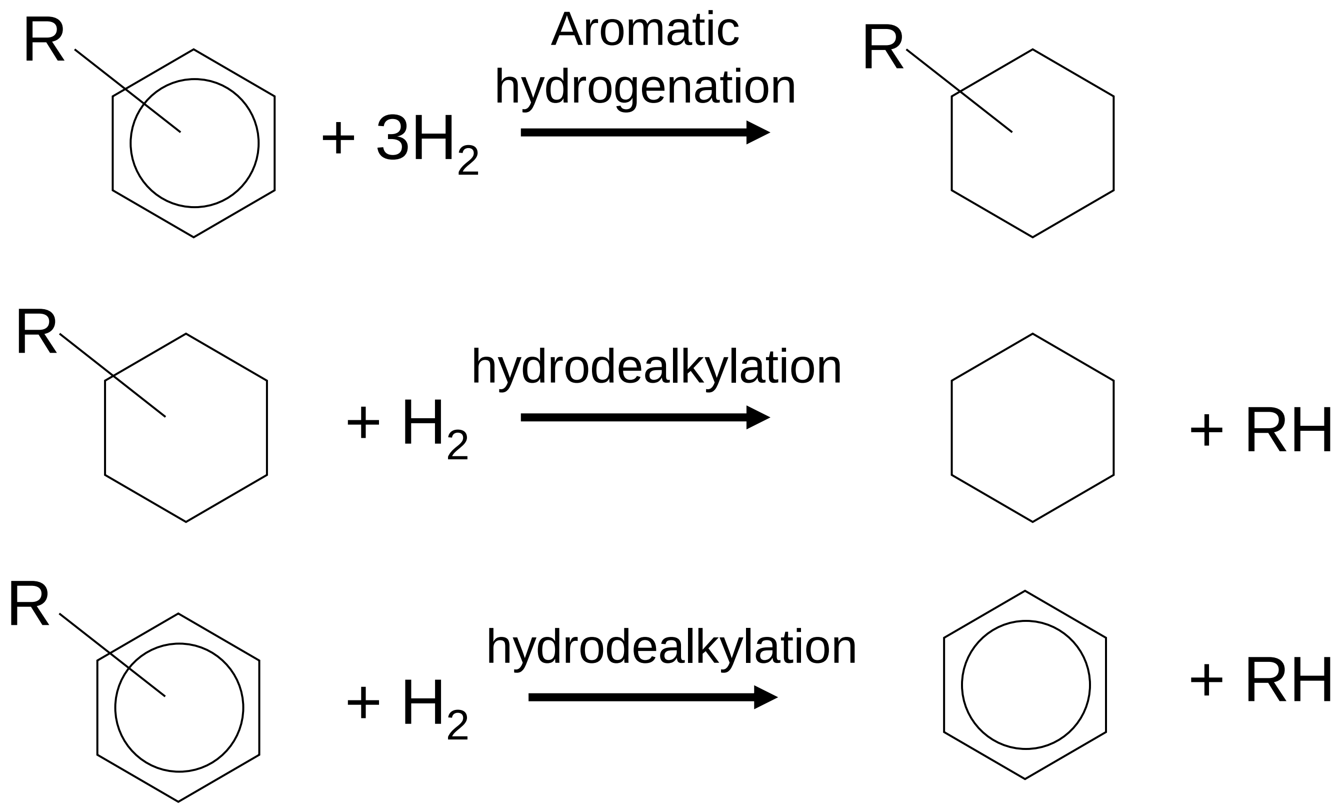
- **C-C bond rupture and hydrogen addition** on two function catalysts

- **C-C bond rupture and hydrogen addition**
  HDT on active centers *(hydrogenolysis)*

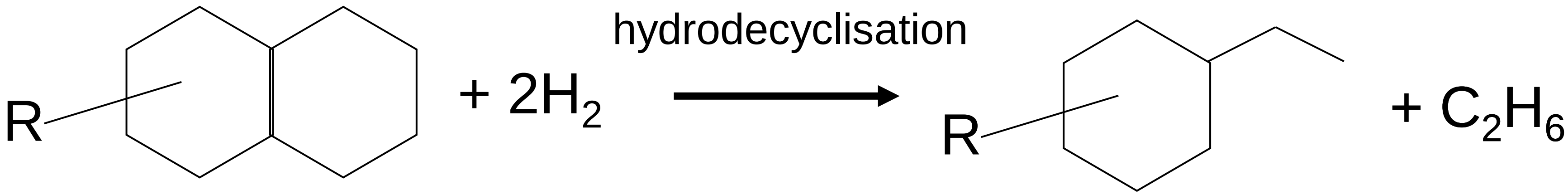
- **Non catalytic: C-C bond radical rupture** and hydrogen addition *(hydropyrolysis)*

- Other reactions

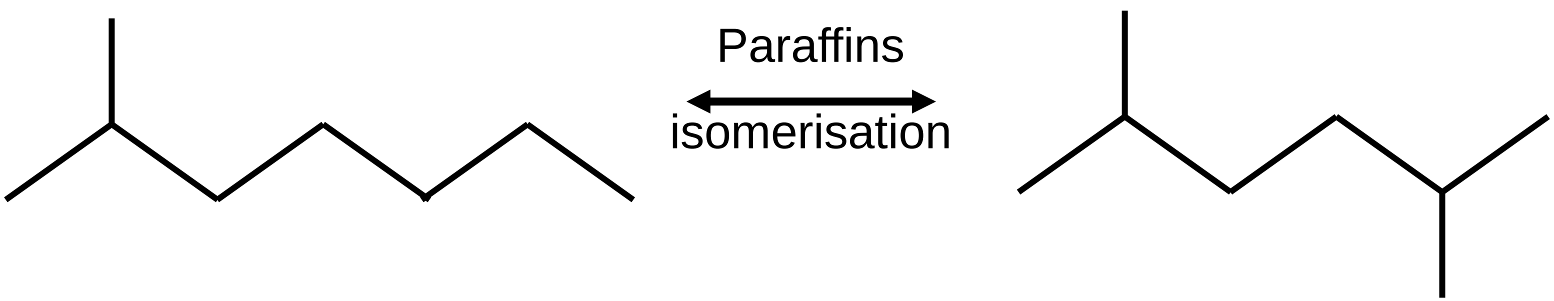
HDT and HCK reactions



HDT and HCK reactions



$$C_nH_{2n+2} \quad + \quad H_2 \xrightarrow[\text{hydrocracking}]{\text{Paraffins}} C_aH_{2a+2} \quad + \quad C_bH_{2b+2} \qquad (a + b = n)$$



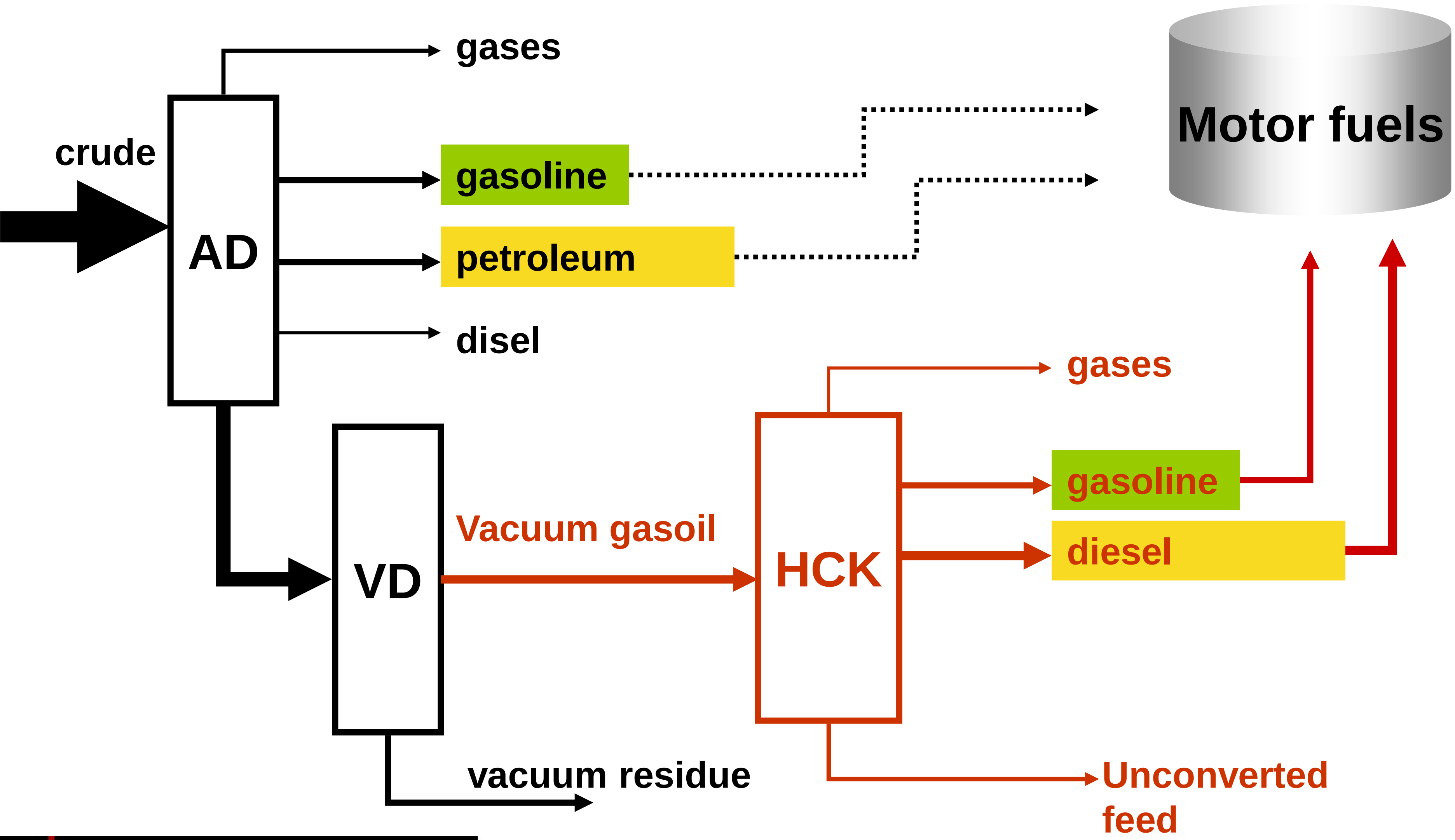
Feed to the HCK plant: vakuum distillate (VGO)

Typical values in case of REB crude

Parameter, unit	Range	Typical value
Density, @20˘C, kg/m3	905-921	915
Nitrogen, wt. ppm	1200-1600	1350
Sulphur, wt. ppm	1,7-2,0	1,85
CCT, wt. %	0,03-0,25	0,13

- **Catalyst poisons:**
  - Basic nitrogen compounds
  - Metals (**V, Ni,** Fe, Na, Cu, Pb, As)

Overall HCK scheme



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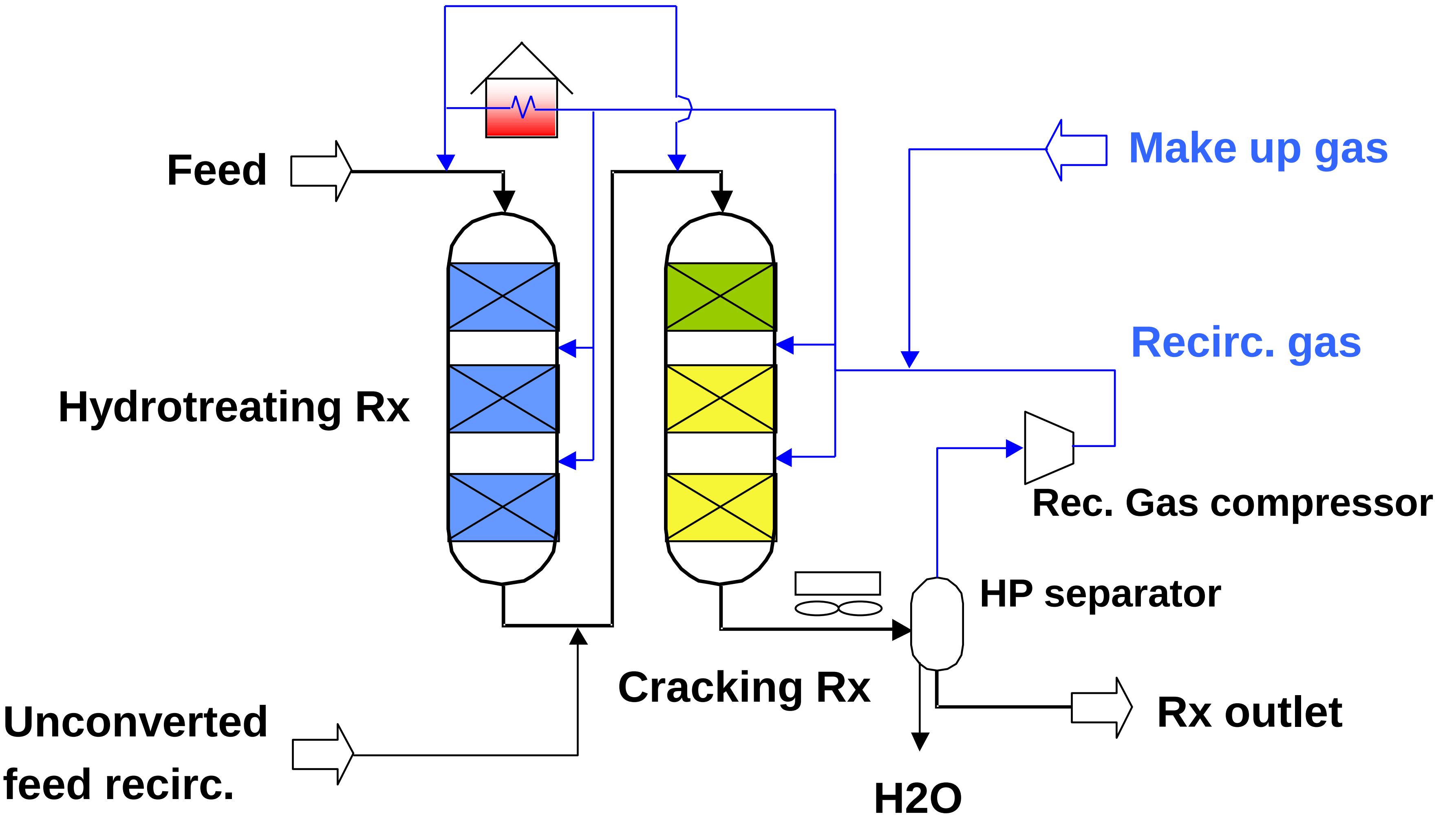
HCK reactor system: simplified scheme



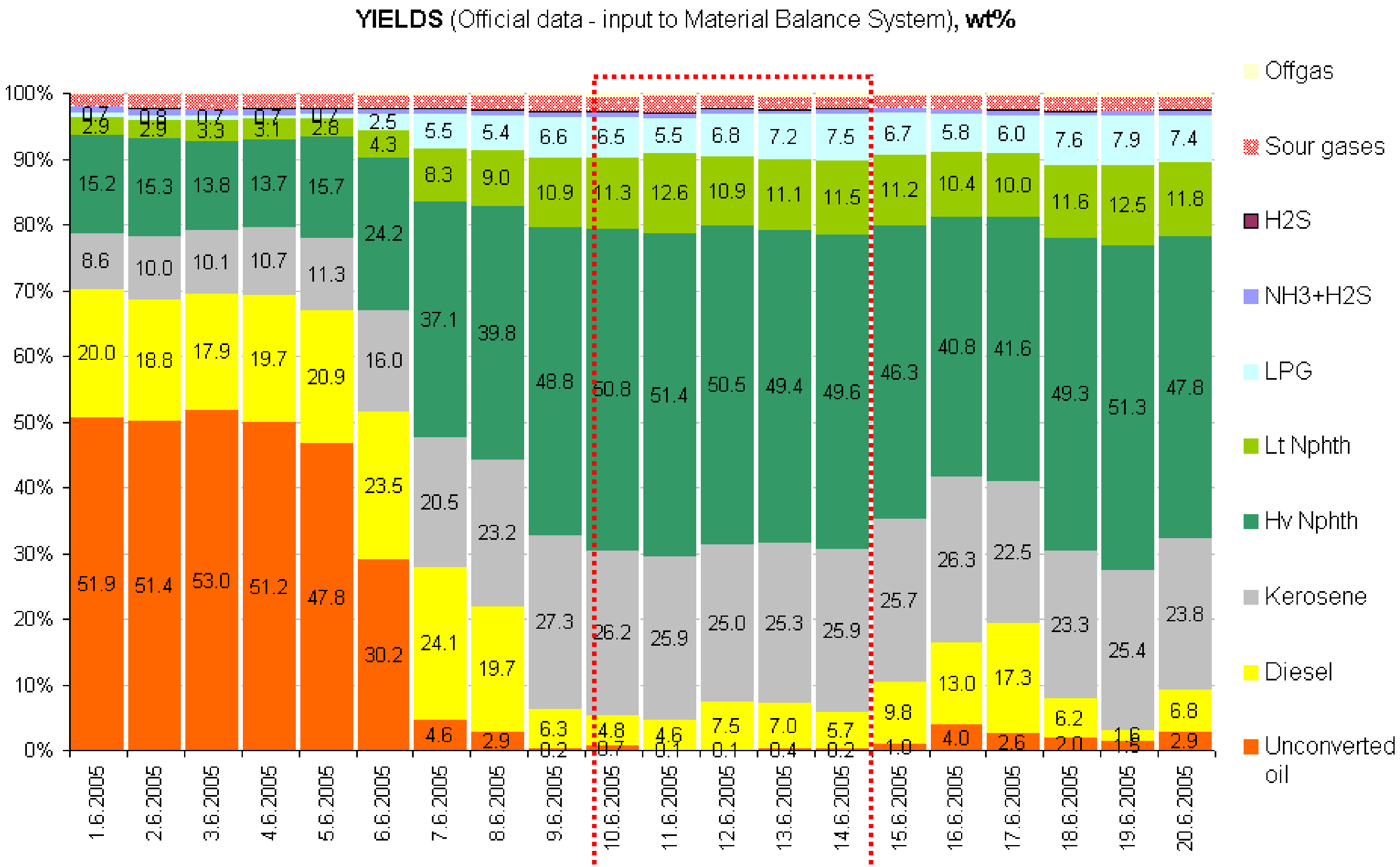
Different HCK designs

- “Once Through”
  (without recirculation, simple scheme, baseoil production)

- Single step, **UCO (UnConverted Oil)** recirculation
  main fractionator bottom recirculation
  ↑ distillate yields, conversion ~ 30-60%
  ↑ energy consumption

- Double step, **UCO** recirculation
  separation of reaction steps, complex scheme
  ↑ investment cost
  ↑ yields, conversion ~ 100%
  ↑ energy consumption

The BR VGO HCK Unit



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Conversion processes – Residue upgrading

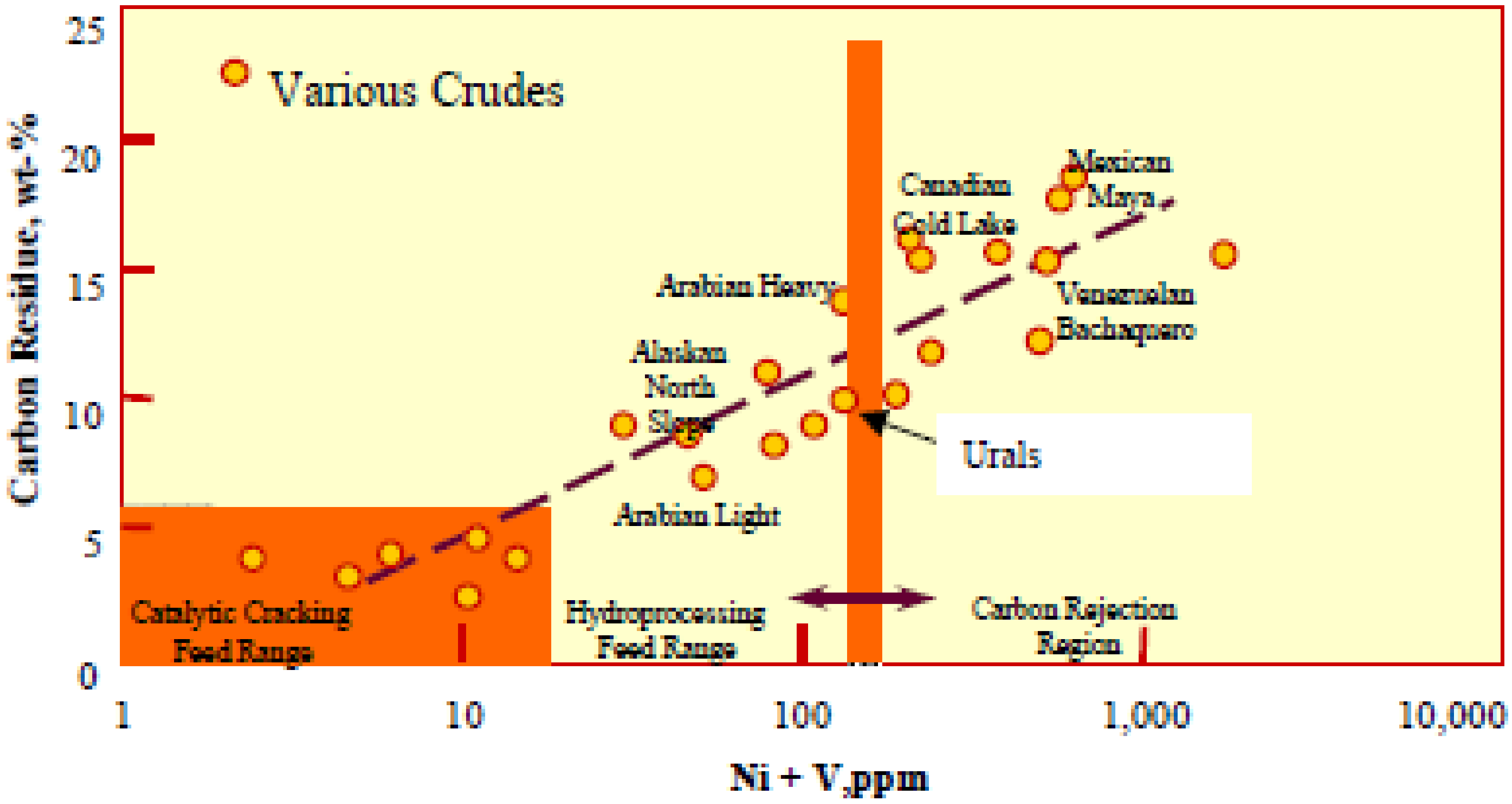
Feed:

Vacuum residue

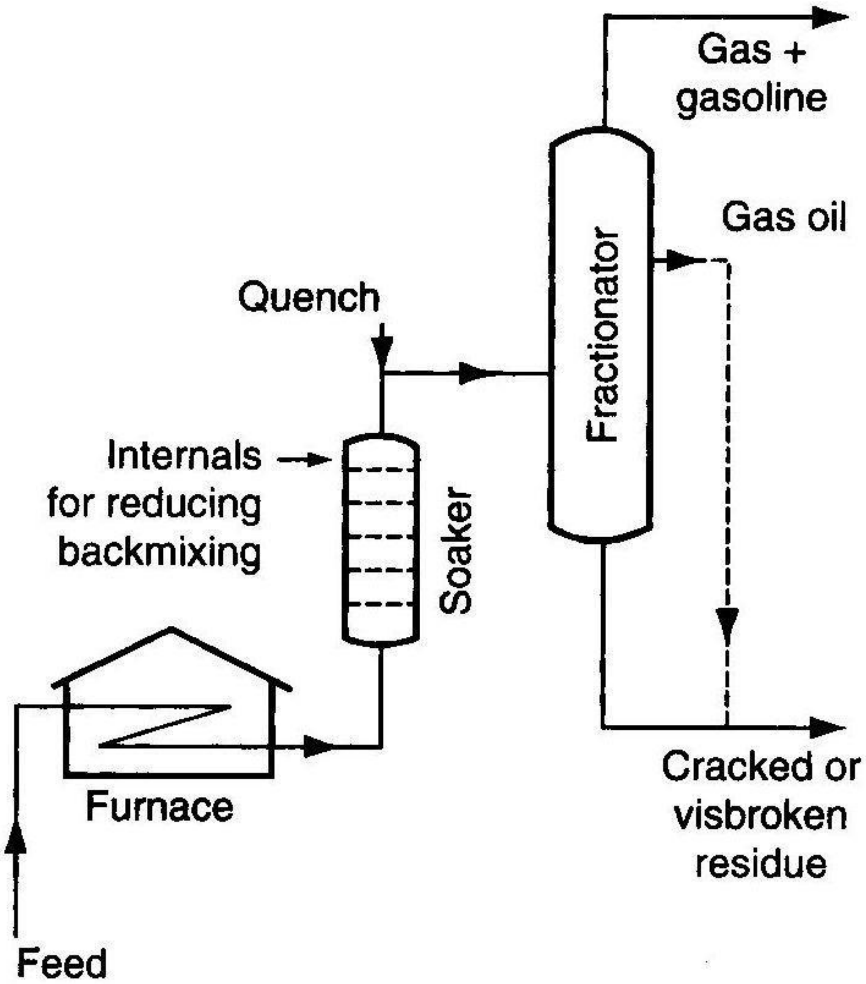
Residue upgrading processes

- **Non catalytic**
  - Solvent asphalt removal
  - ***Thermal***
    - **Delayed coking**
    - Fluid coking
    - Flexicoking
    - Visbreaking
    - Gasification
- **Catalytic**
  - Residue fluid catalytic cracking (RFCC)
  - ***Residue hydrocracking***
    - fixed bed
    - ebullated bed

Carbon removal or hydrogen introduction



Residue upgrading – Visbreaking



Goal: viscosity reduction of fuel oil like reidues

Feed: fuel oil components

Products: fuel oil, gasoline, diesel components (needs desulphurisation)

Process parameters:

Temperature: 450 - 500 °C

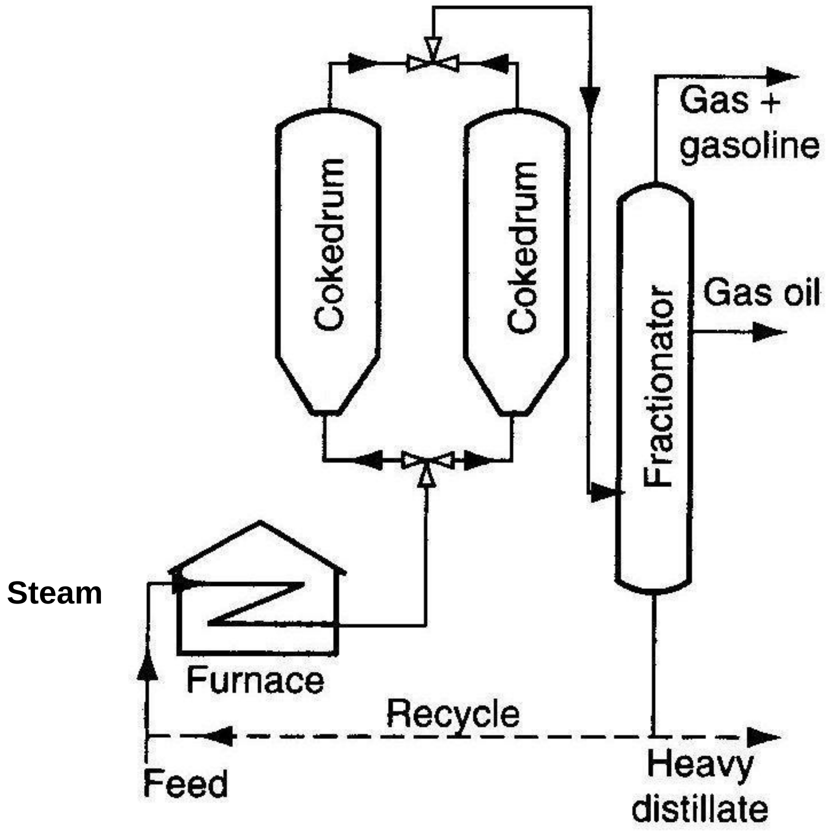
Pressure: 5 – 20 bar

Yield structure:

• H_2S	0,2 %
• Fuel gas	0,7 %
• C_3/C_4	1,1 %
• Gasoline	4,1 %
• Diesel	11,7 %
• Residue	82,2 %

Residue upgrading – Delayed coking

Residue upgrading – Delayed coking



Goal: production of valuable lighter components (need hydrotreating), while forming solid coke residue

Feed: vaccum residue

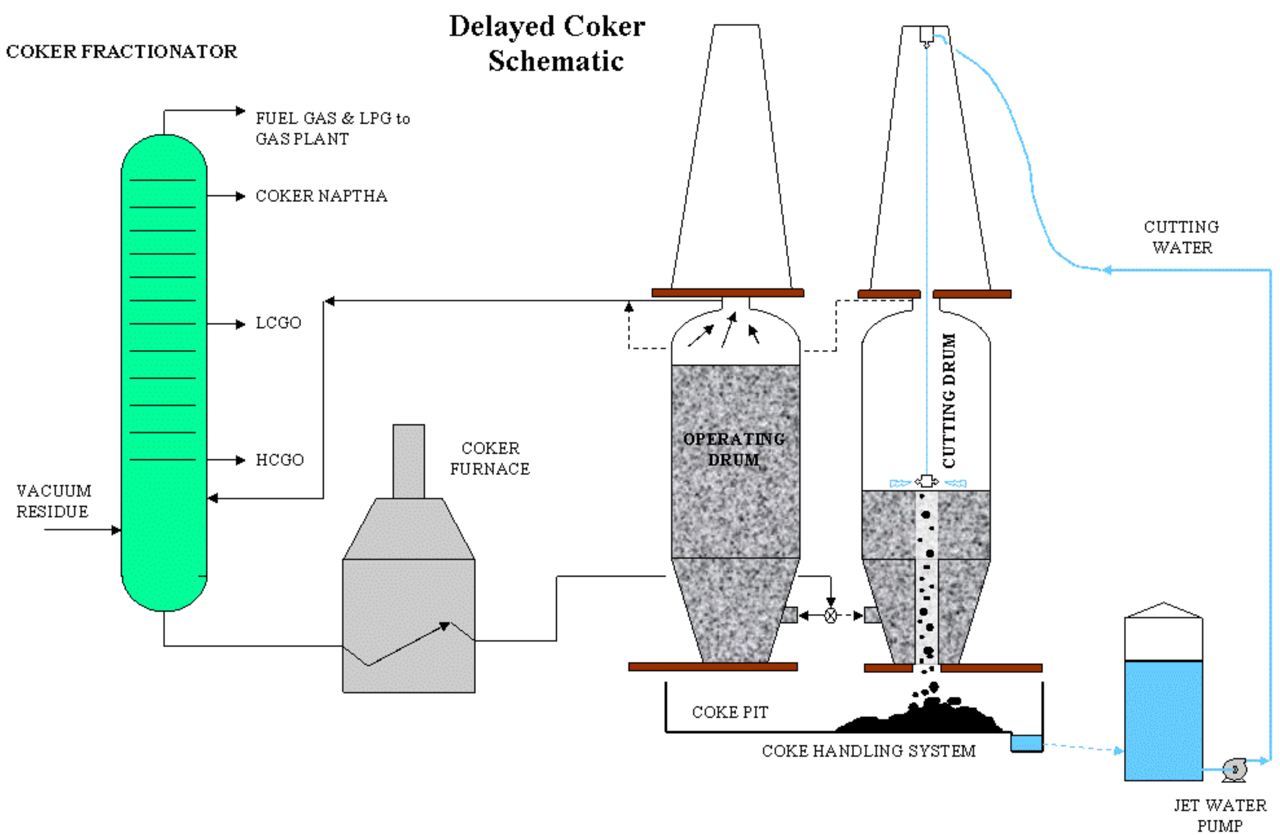
Products: gases, gasoline, diesel, coke

Process parameters:

Temperature: 480 - 520 °C

Pressure: 1 – 5 bar

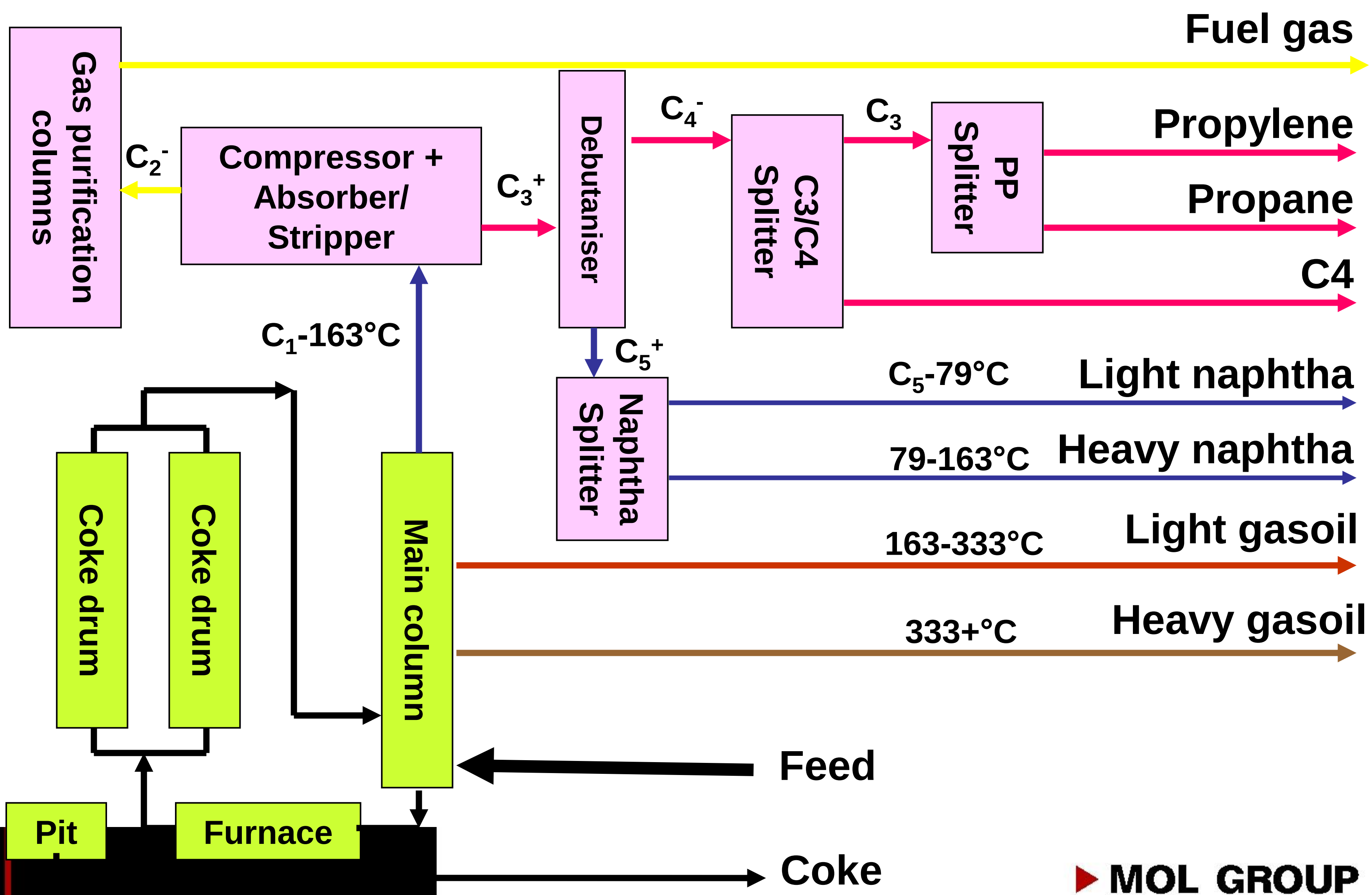
• MARADÉKFELDOLGOZÁS / KÉSLELTETETT KOKSZOLÁS



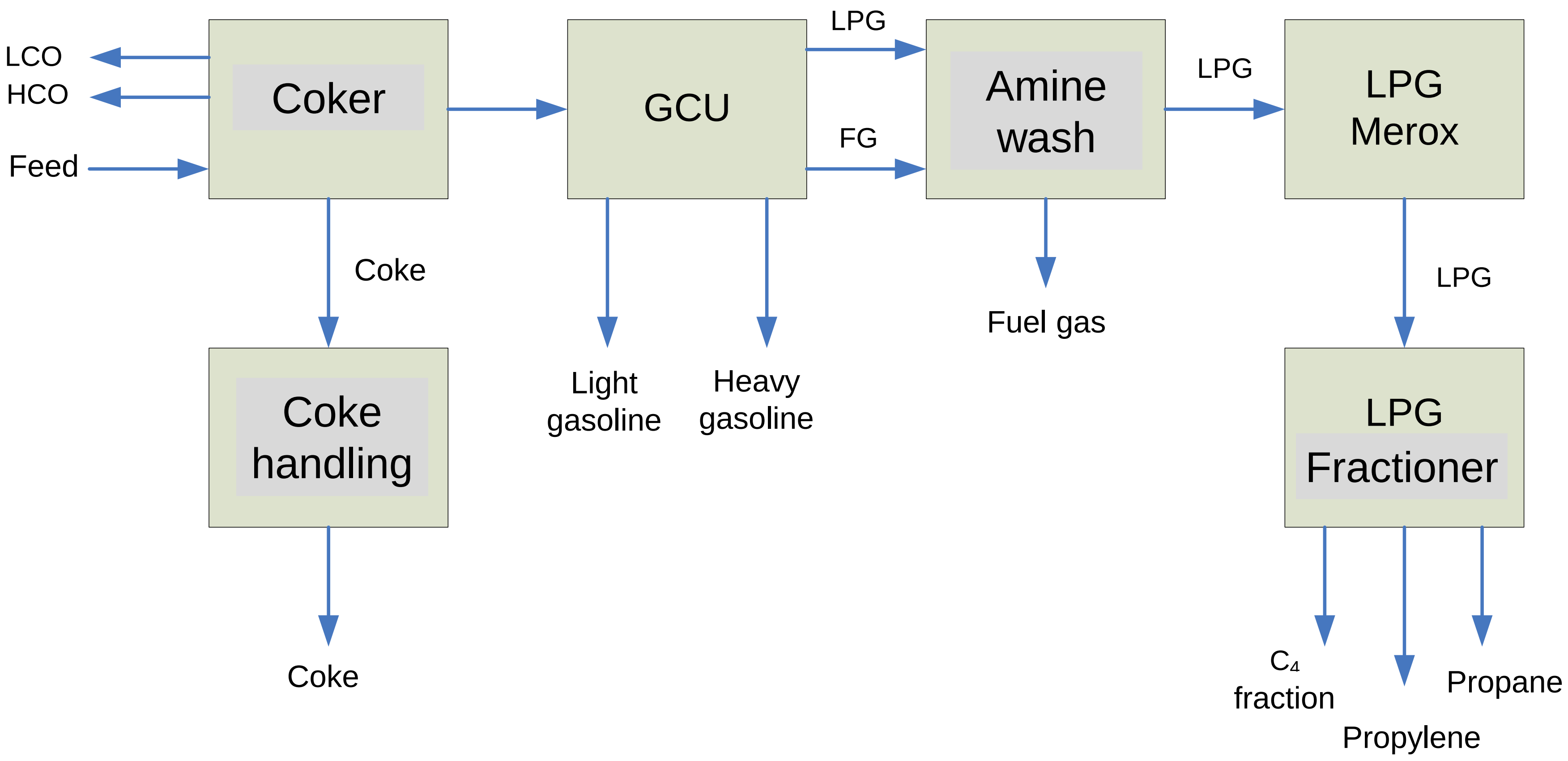
Residue upgrading – Delayed coking

- Heaviest components of the feed are converted to solid coke due to very complicated series of reactions (aliphatic C-C bond rupture, isomerisation, ring formation, hydrogen removal, dehydrogenation, polymerization of unsaturated compounds, dealkylation and condensation of aromatic ring), while majority of the feed is converted to valuable lower boiling range components.
- The coking procedure is so complicated, that it cannot be depicted with concrete chemical reactions. However, three main steps may be derived:
  - The feed, flowing through the heater pipes, is partially evaporated and mildly cracked (viscosity breaking);
  - The hydrocarbon vapors are further cracked, while travelling through the coke drum;
  - The liquid, entrapped in the coke drum, are converted to coke and vapors, via polymerization and cracking reactions.
- Product yield and quality are determined by three parameters:
  - Temperature
  - Pressure
  - Recirculation rate.

Delayed coking – Scheme



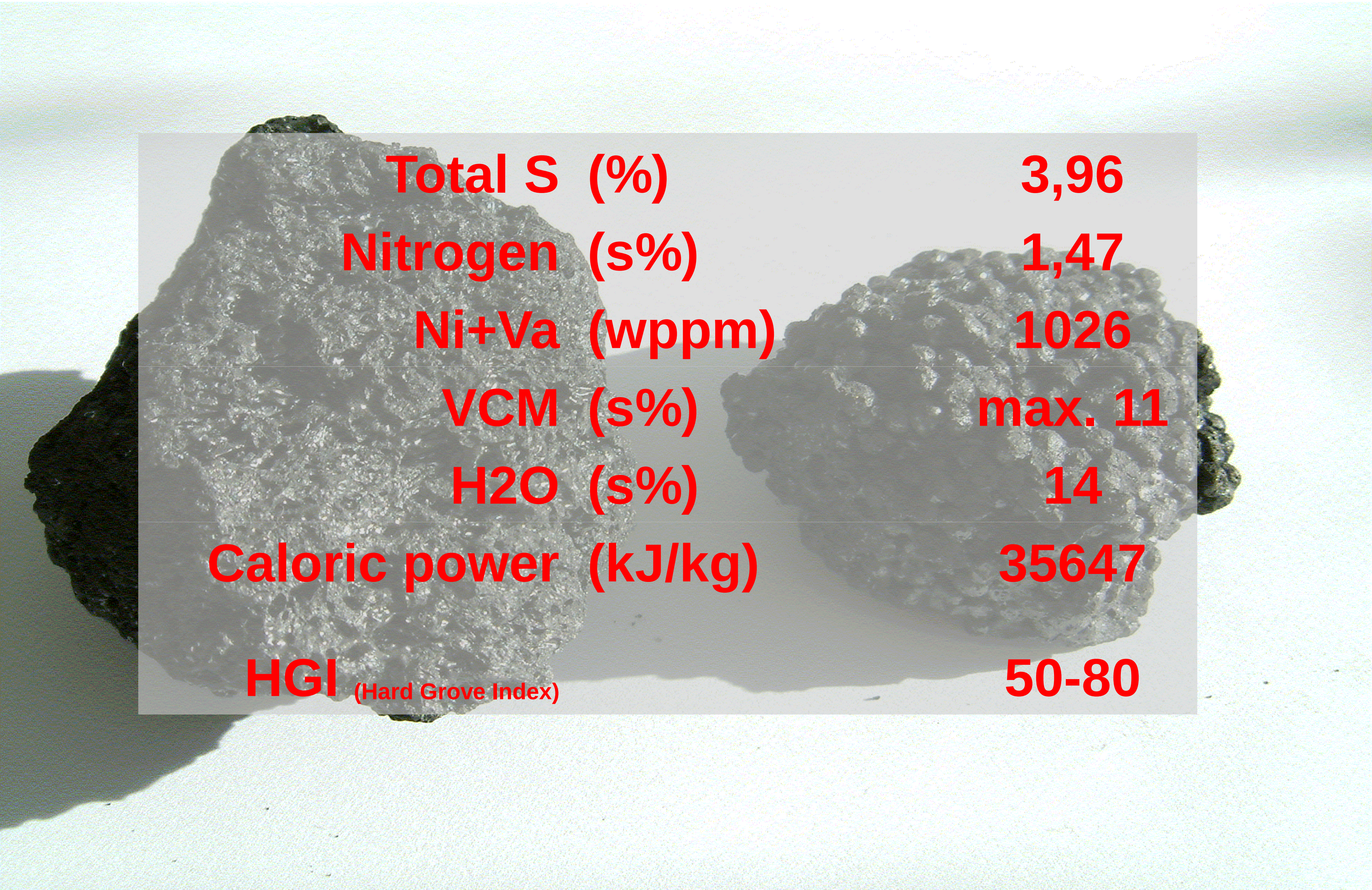
Delayed coking – Blockscheme



Delayed coking – Yields

• Fuel gas	3,5 %
• C3	3,8 %
• C4	1,0 %
• Lt gasoline	2,7 %
• Hvy gasoline	8,0 %
• Gasoil	15,6 %
• V. distillate	38,7 %
• Coke	24,6 %

Delayed coking – Coke parameters



Total S	(%)	3,96
Nitrogen	(s%)	1,47
Ni+Va	(wppm)	1026
VCM	(s%)	max. 11
H_2O	(s%)	14
Caloric power	(kJ/kg)	35647
HGI (Hard Grove Index)		50-80

Residue upgrading – Delayed coking


Thank you for your attention!