HYDROCARBON PROCESSING TECHNOLOGIES

CONVERSION TECHNOLOGIES

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Polyol Product Development and Technical Service

Budapest, 25 October 2023

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CRUDE PROCESSING

Economic rationale

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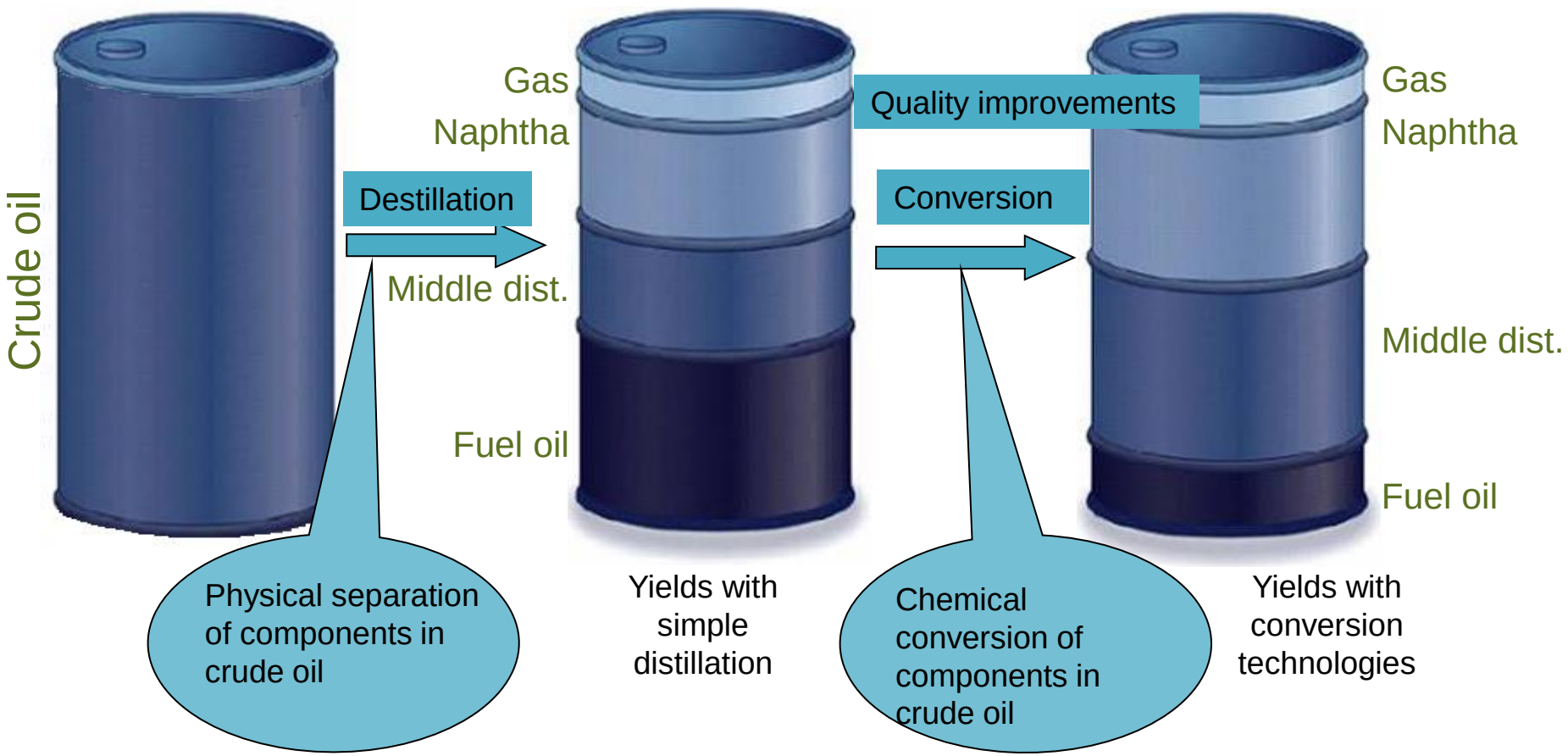
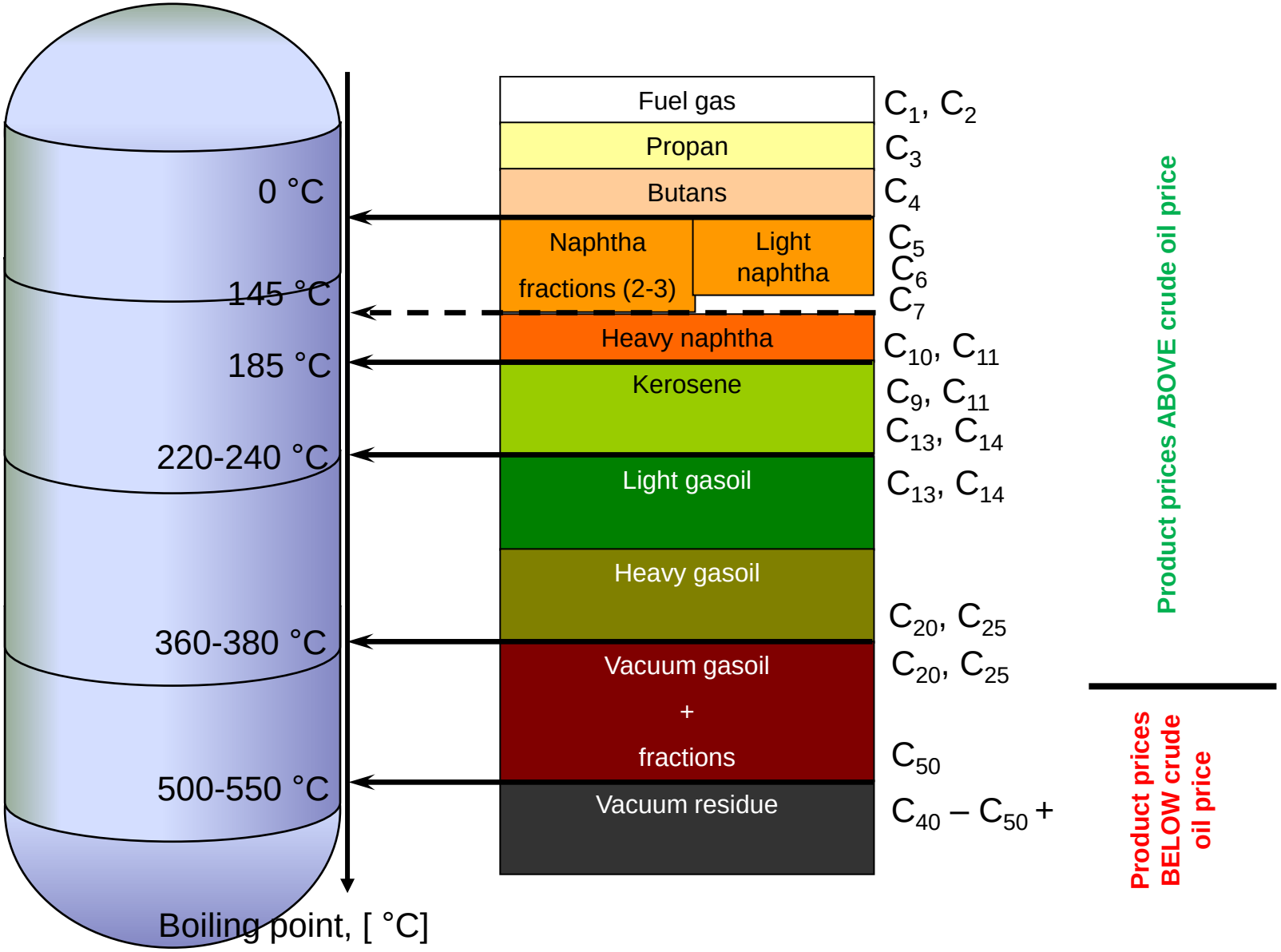
AIM OF CRUDE PROCESSING

Provide product structure in line with market demands



The whole process is crude oil refining

CRUDE OIL FRACTIONS



HOW TO MEET DEMANDS?

CRUDE OIL DIVERSIFICATION

SELECTION OF THE MOST SUITABLE CRUDE

CONVERSION INCREASE IN REFINERY:

CHANGING REFINERY YIELDS IN POSITIVE DIRECTION BY MODIFICATION OF PROCESSING TECHNOLOGY SCHEME

CRUDE OIL DIVERSIFICATION

Alternative crudes

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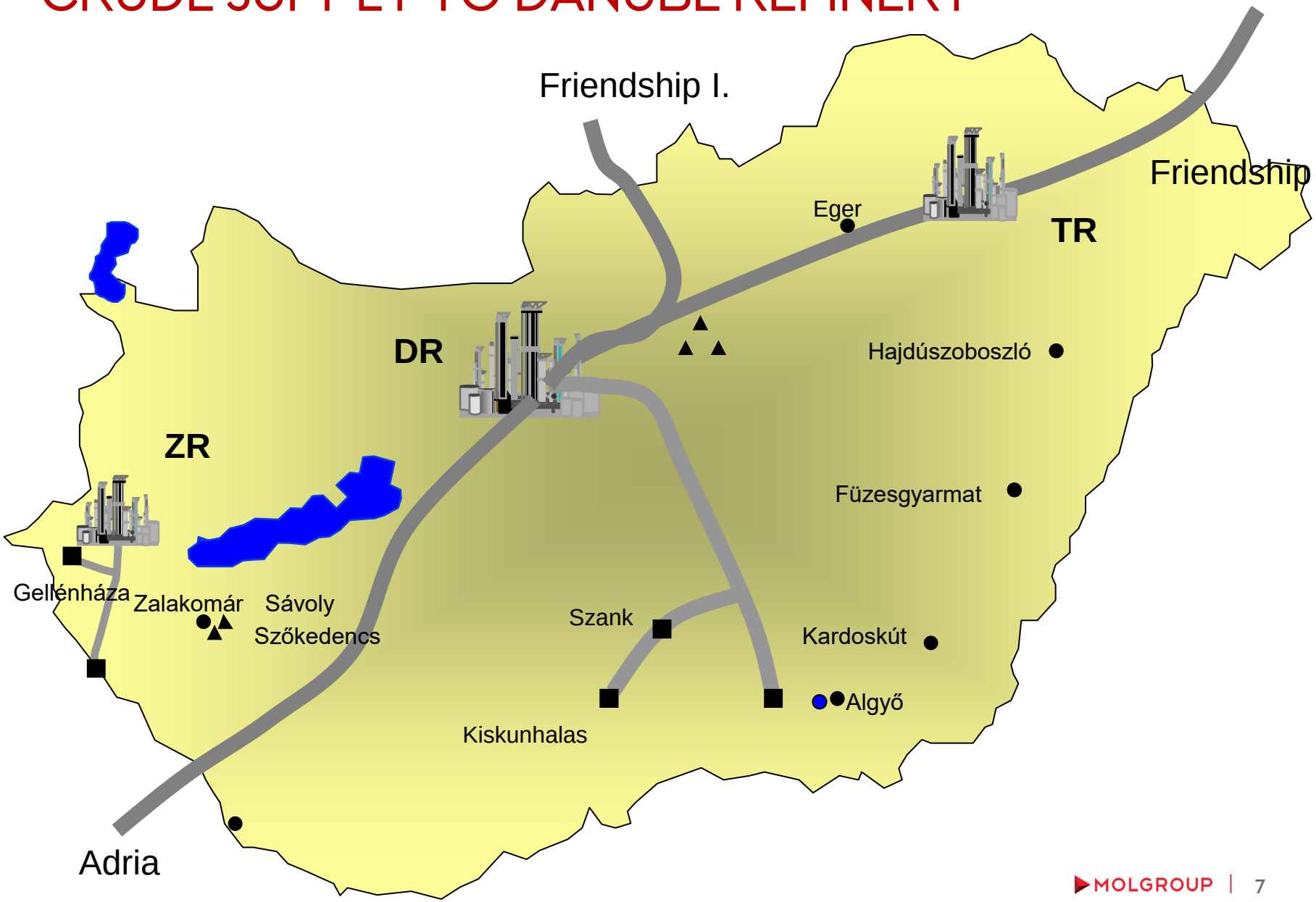
CRUDE SUPPLY TO DANUBE REFINERY



REFINERY CONVERSION INCREASE

CONVERSION
TECHNOLOGIES

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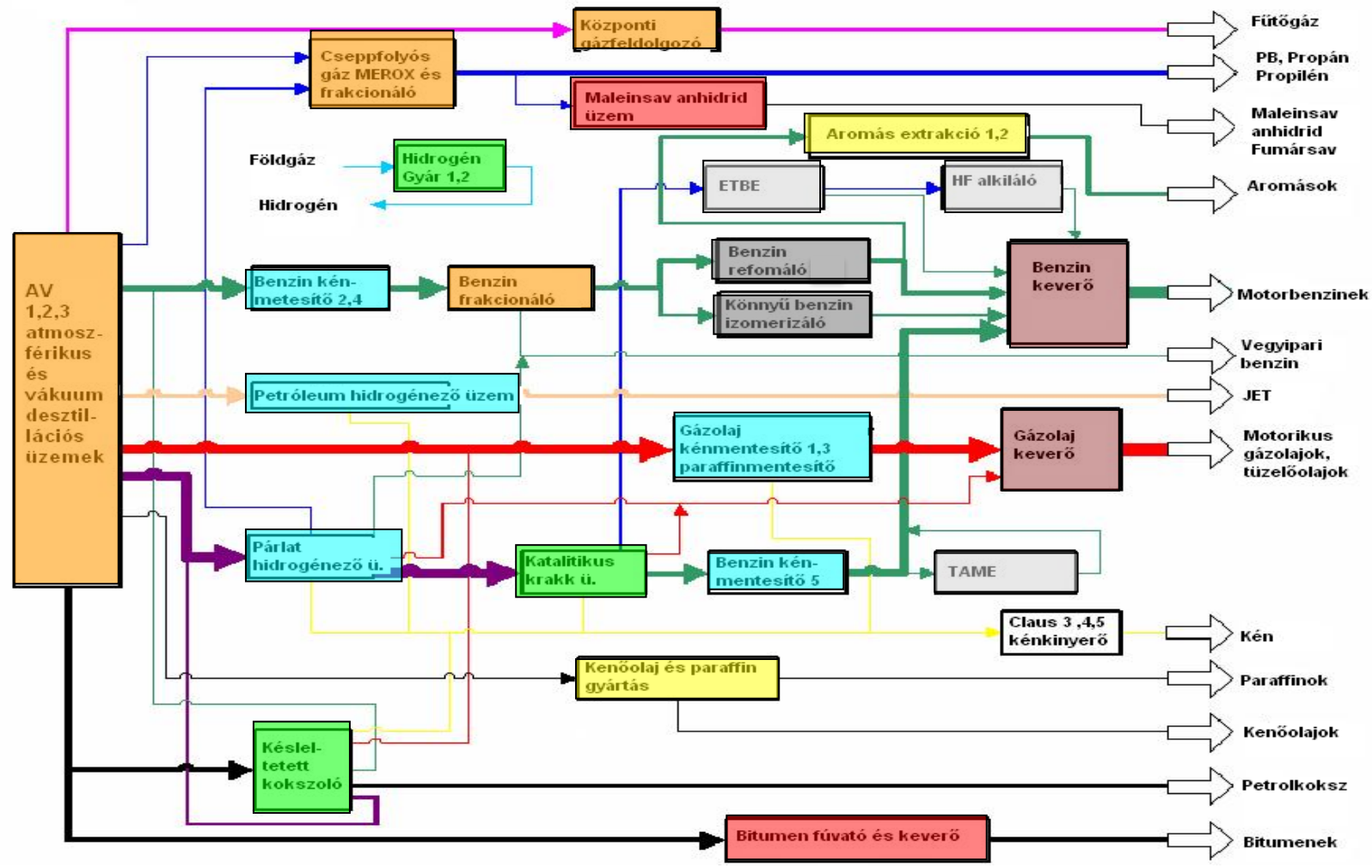
CONVERSION TECNOLOGIES

DRIVER:

ENSURE BEST MATCH BETWEEN MARKET DEMANDS AND REFINERY YIELDS
(VOLUME DEMANDS/FLEXIBILITY)

PRODUCE THE HIGHEST AMOUNT OF VALUABLE PRODUCTS FROM THE CRUDE
(ECONOMICS)

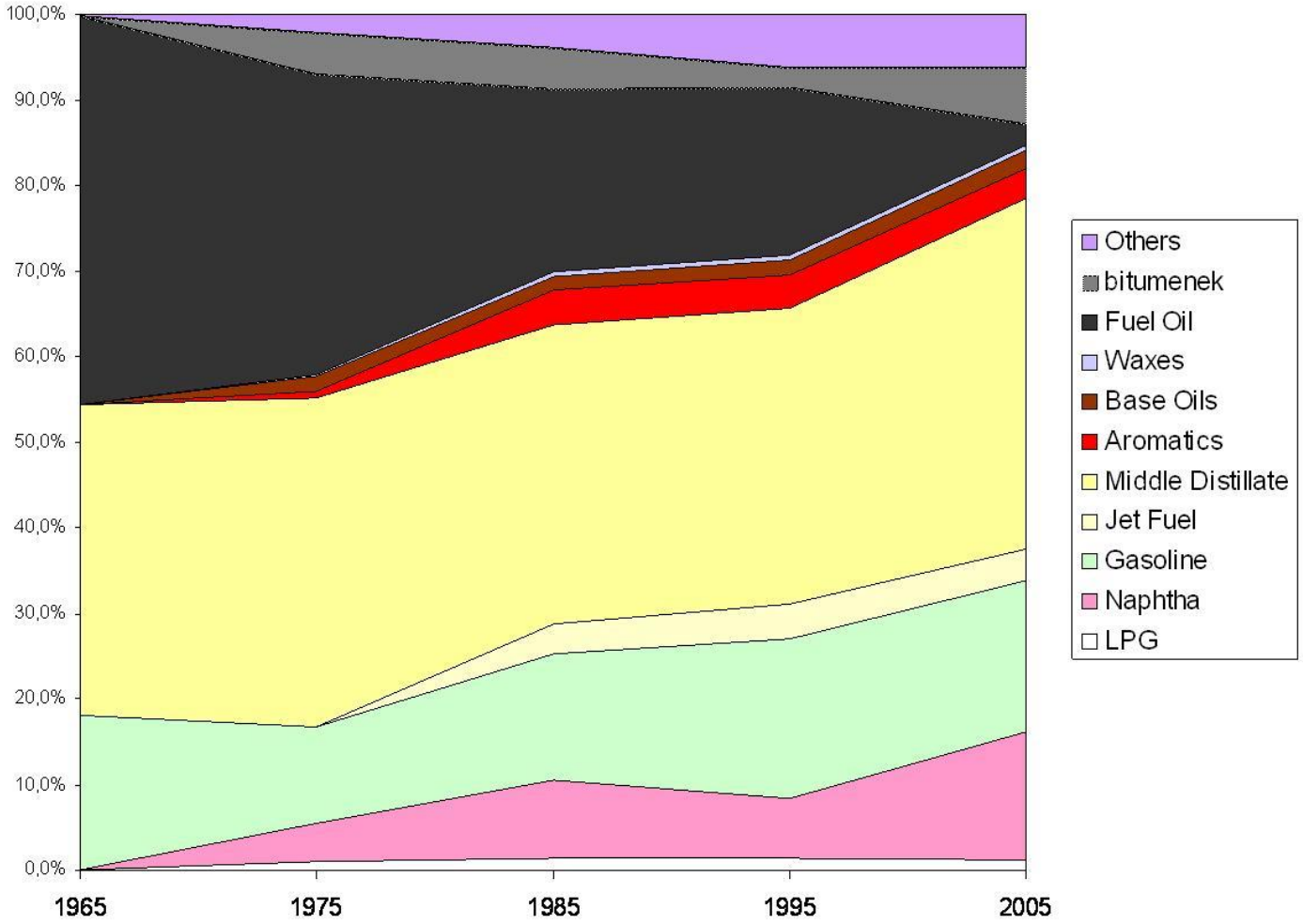
TYPICAL REFINERY SCHEME (DANUBE REF)



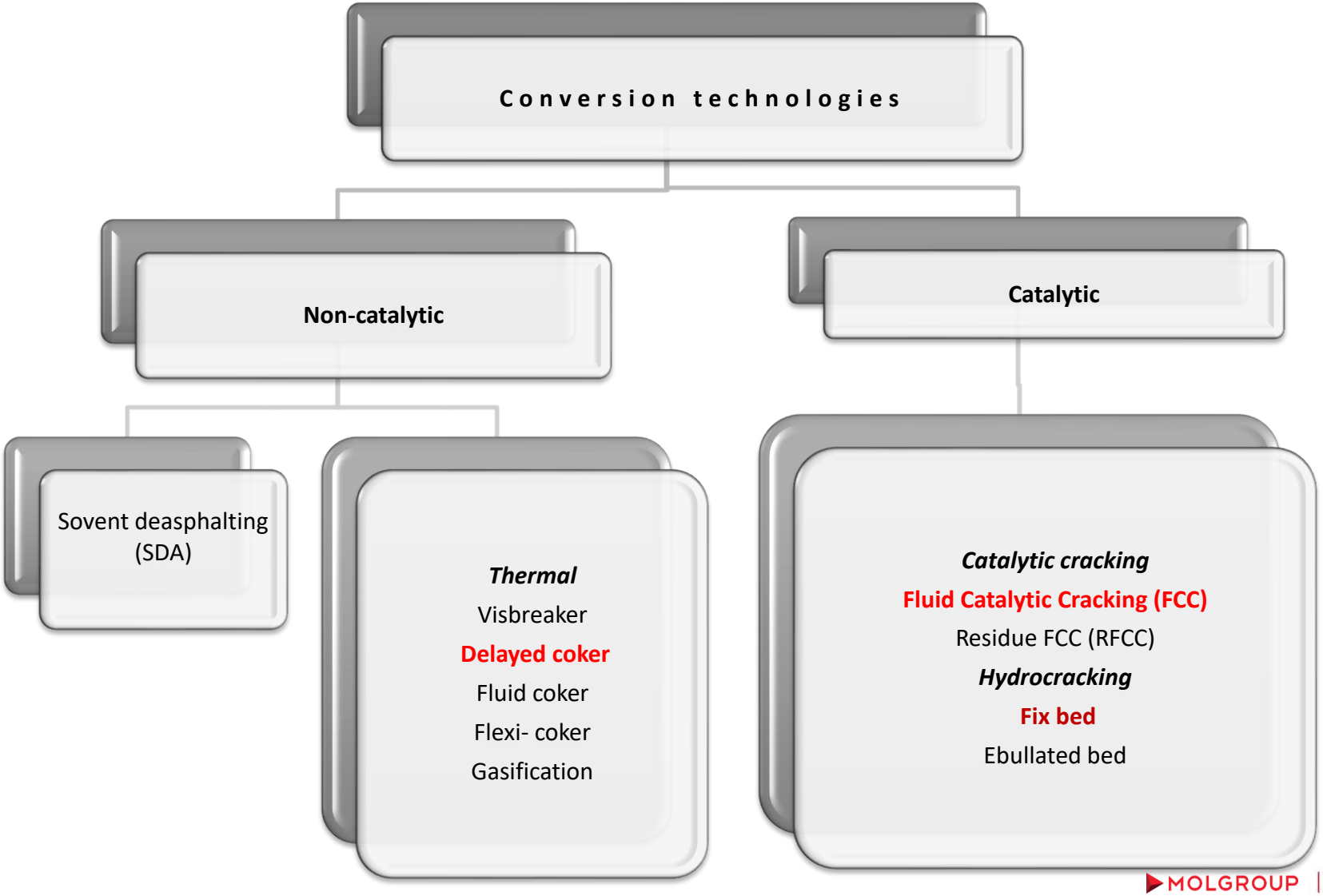
Forrás: MOL

DANUBE REFINERY –YIELDS

Changes in yields between 1965-2005



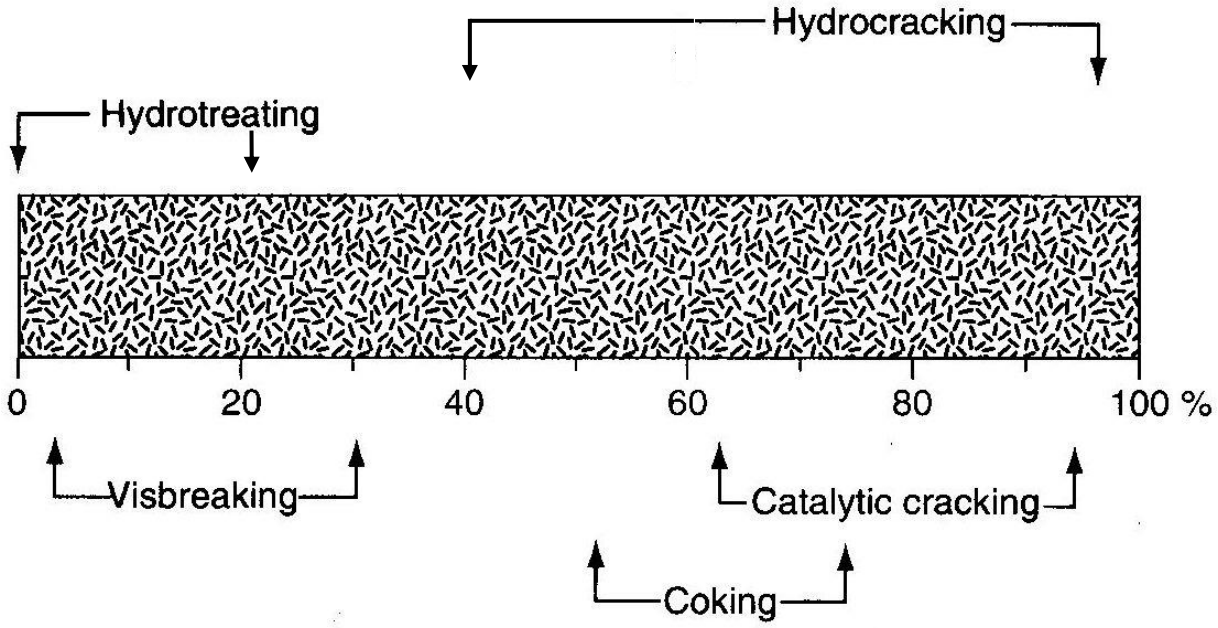
TYPES OF CONVERSION TECHNOLOGIES



CONVERSION TECHNOLOGIES

Aim: increase H/C ratio in molecules

Feed conversion of different technologies:



Hydrogenation

Carbon rejection

Feedstock:

vacuum gasoil

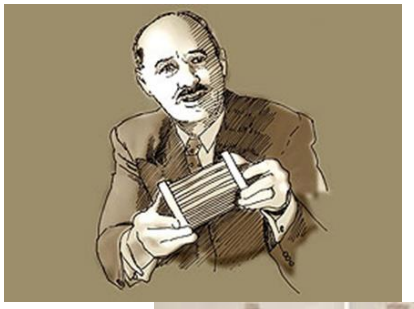
vacuum residue (gudron)

Thermal / Catalytic

CRACKING

1910 Burton thermal cacking

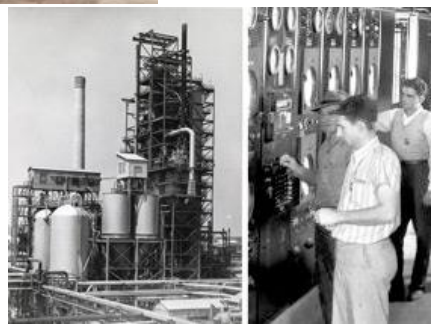
Naphtha from cude



1920 Eugene Jules Houdry

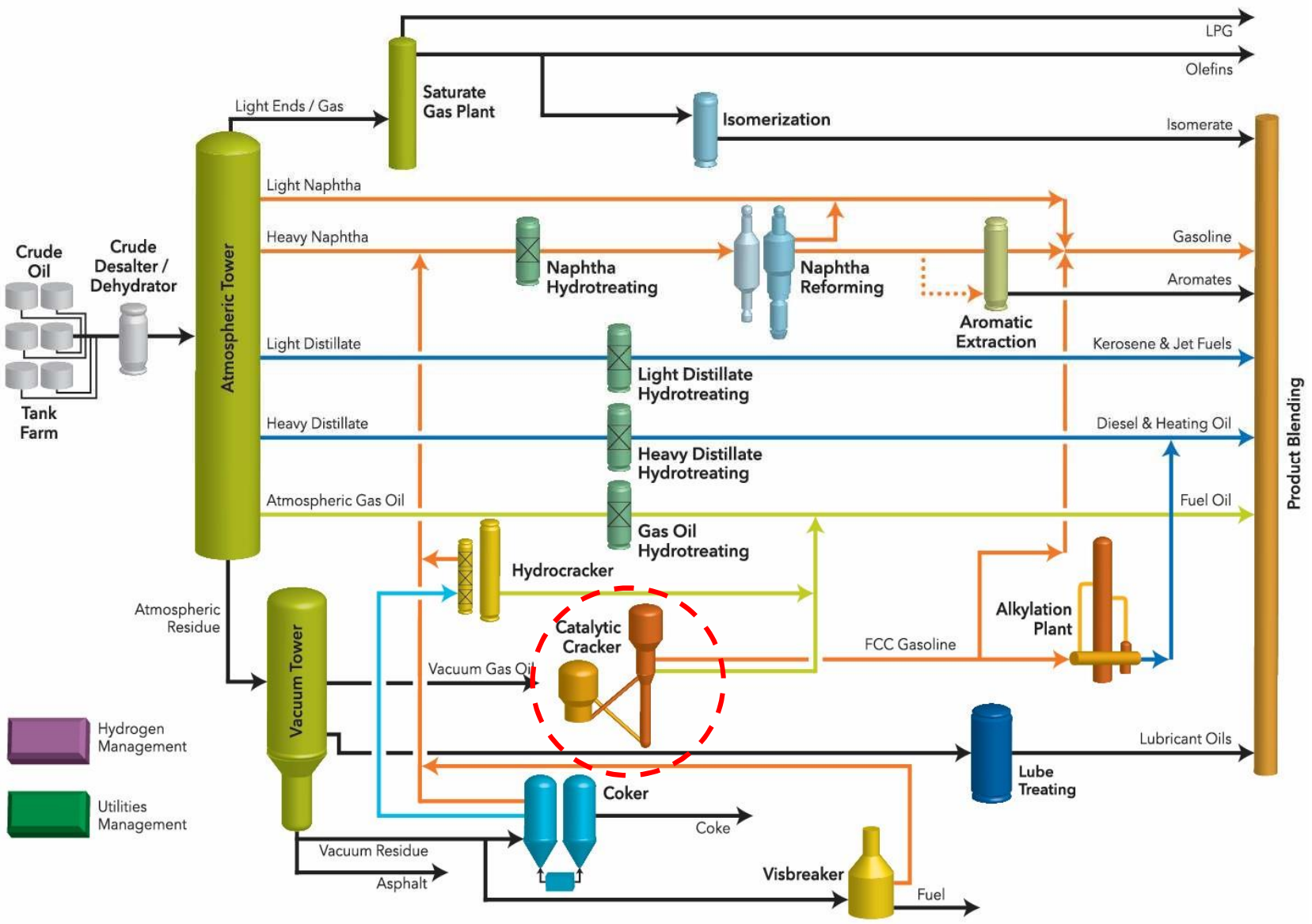
Catalytic process from lignite to naphtha

1936 First cracking unit in New Jersey



1942 First fluid catalytic cracking unit

PLACE OF A CATALYTIC CRACKING UNIT



CONVERSION TECHNOLOGIES / CATALYTIC CRACK

Purpose: cracking of vacuum gasoil – molecular weight and boiling point reduction

Feed: vacuum gasoil

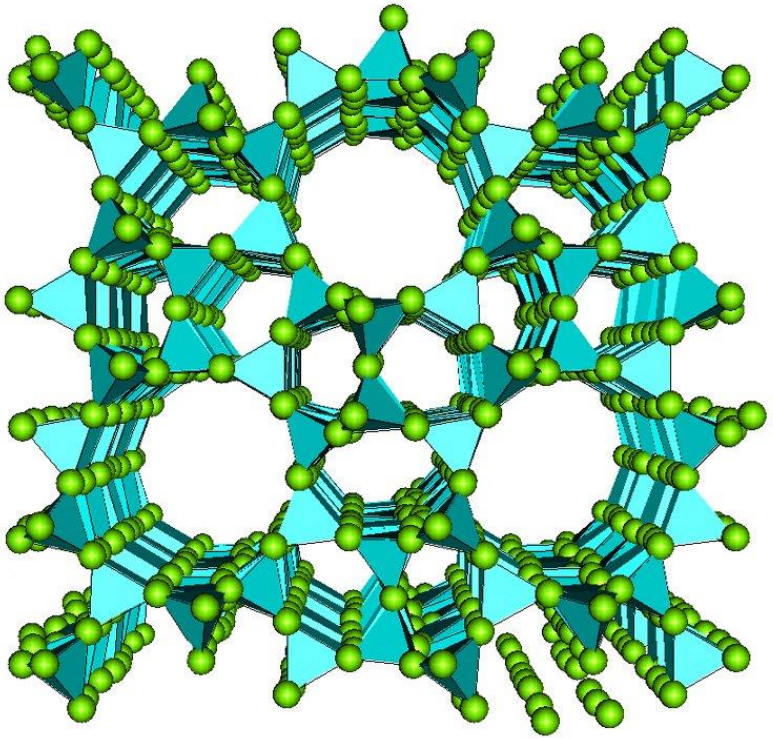
Products: C_3-C_4 mix, cracked naphtha, gasoil (LCO)

Parameters: Temperature: 480 - 540 °C

Pressure: 2 – 4 barg

Catalyst: zeolites (Al_2O_3 - SiO_2)

FCC : Contact time: 1-2 sec



Zeolites: aluminium-silicate crystals with molecular-size pores and channels

CONVERSION TECHNOLOGIES / CATALYTIC CRACK

Pur

Fee

Pro

Par

Pre

Cat

FC

molecular-size pores and channels

CONVERSION TECHNOLOGIES / CATALYTIC CRACK

Purpose: cra
molecu
reducti

Feed: vacuur

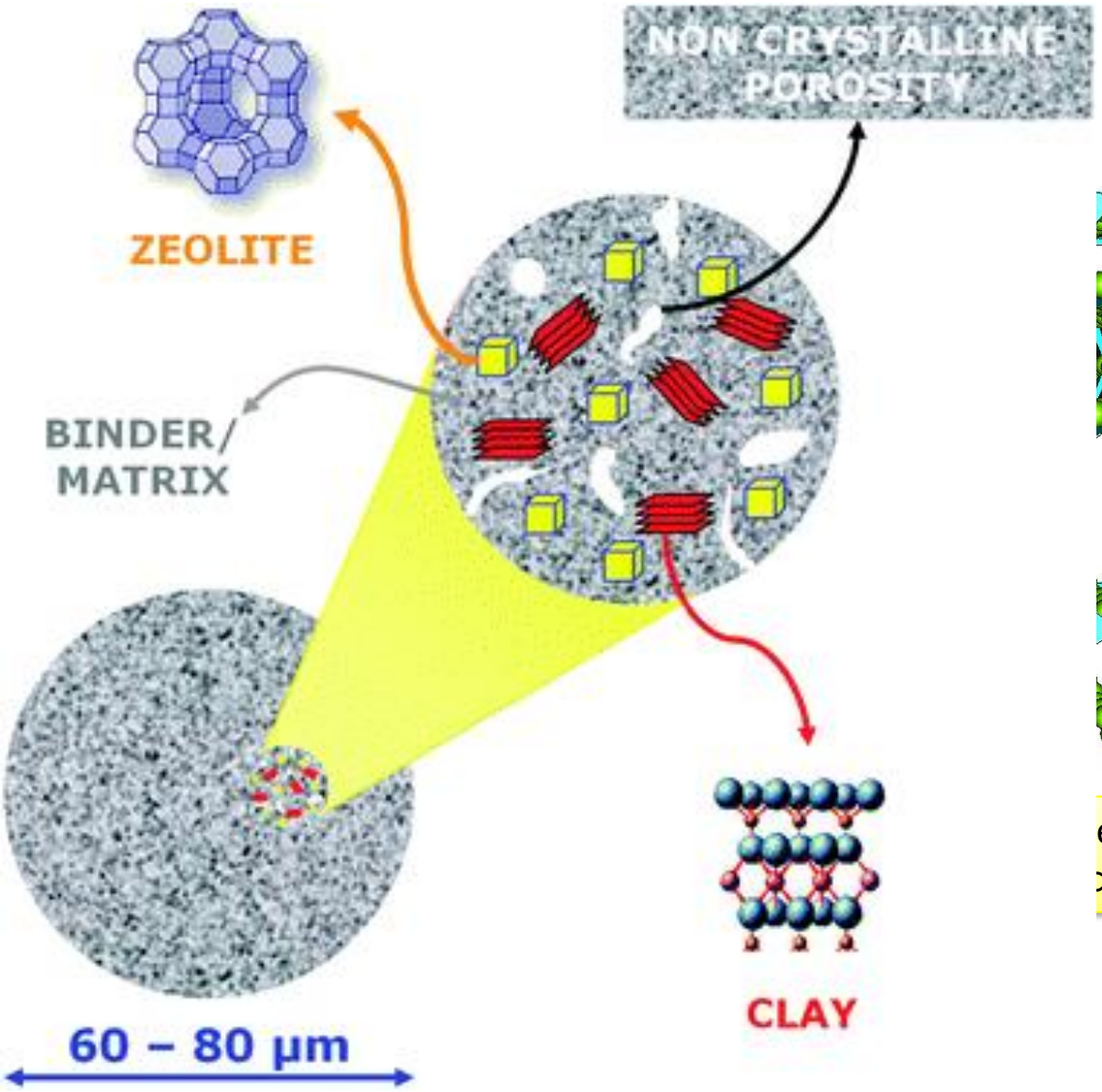
Products: C_3
gasoil (

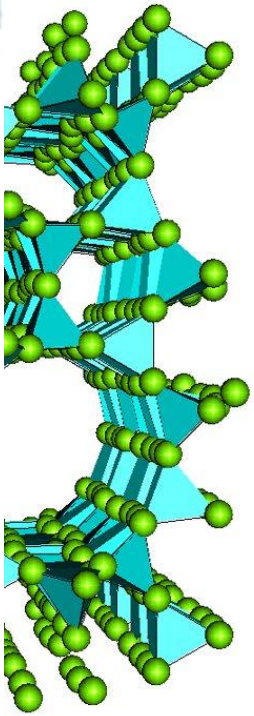
Parameters:

Pressure: 2 –

Catalyst: zeo

FCC : Cont





e crystals with
channels

CONVERSION TECHNOLOGIES / CATALYTIC CRACK

Purpose: crackin
molecular w
reduction

Feed: vacuum ga

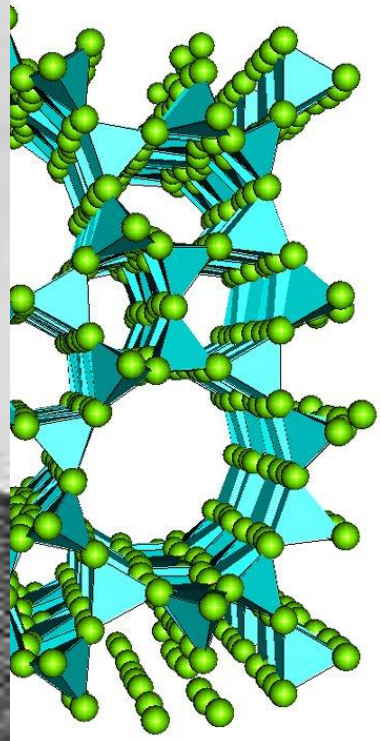
Products: C_3-C_4 r
gasoil (LCC

Parameters: Tem

Pressure: 2 – 4 ba

Catalyst: zeolite

FCC : Contact



-silicate crystals with molecular-size pores and channels

Rabó Gyula
1924-2016

REACTIONS OF CATALYTIC CRACKING

Reactions

:

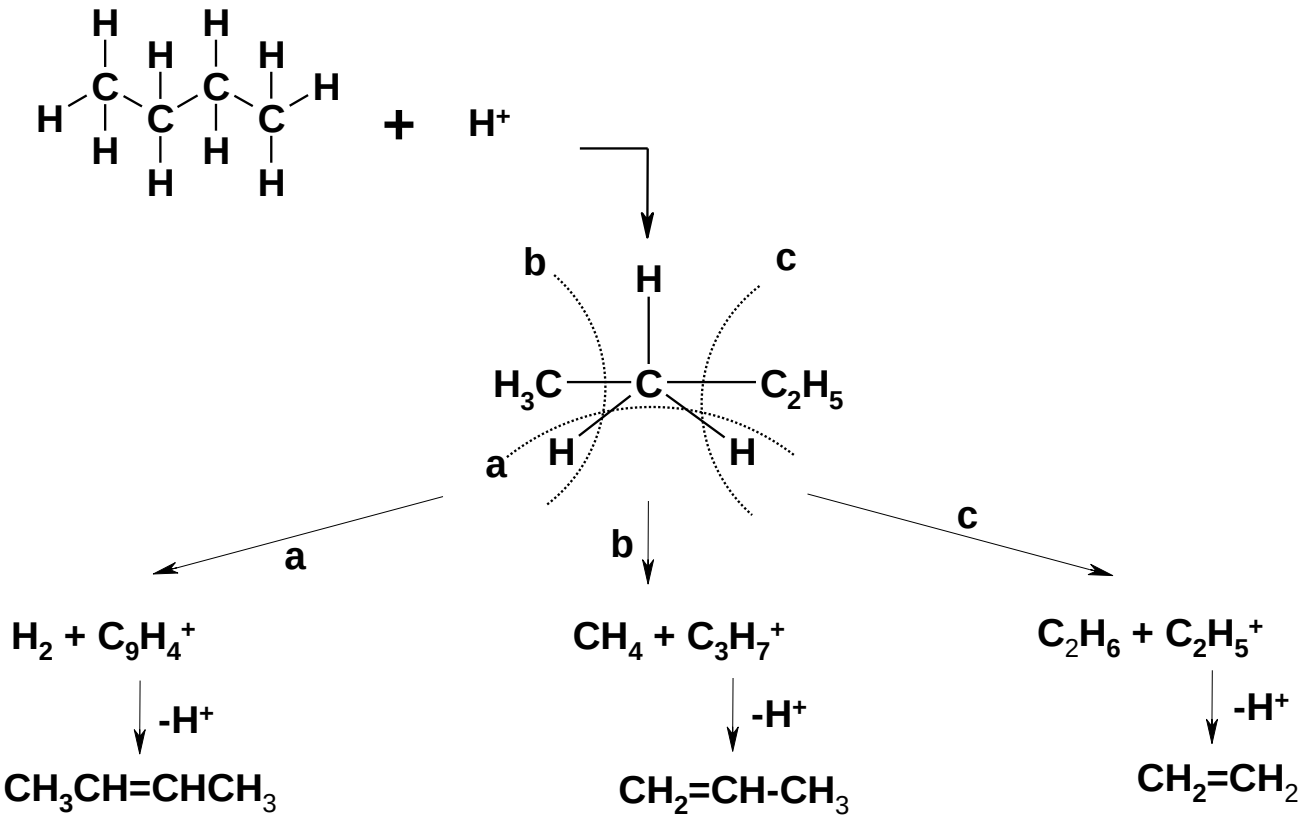
Catalytic cracking
Thermal cracking
De-hydrogenation
Hydrogen transfer
Polymerisation

Effects

- Yields
- Components
  (olefin, armatics)
- Quality
  (octane number, cetane number)

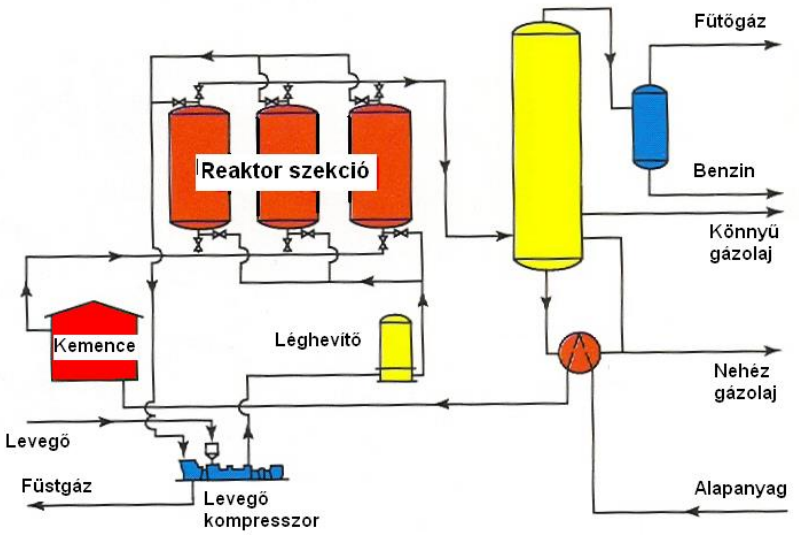
CONVERSION TECHNOLOGIES / FLUID CATALYTIC CRACK (FCC)

Main reactions:



CONVERSION TECHNOLOGIES / FCC

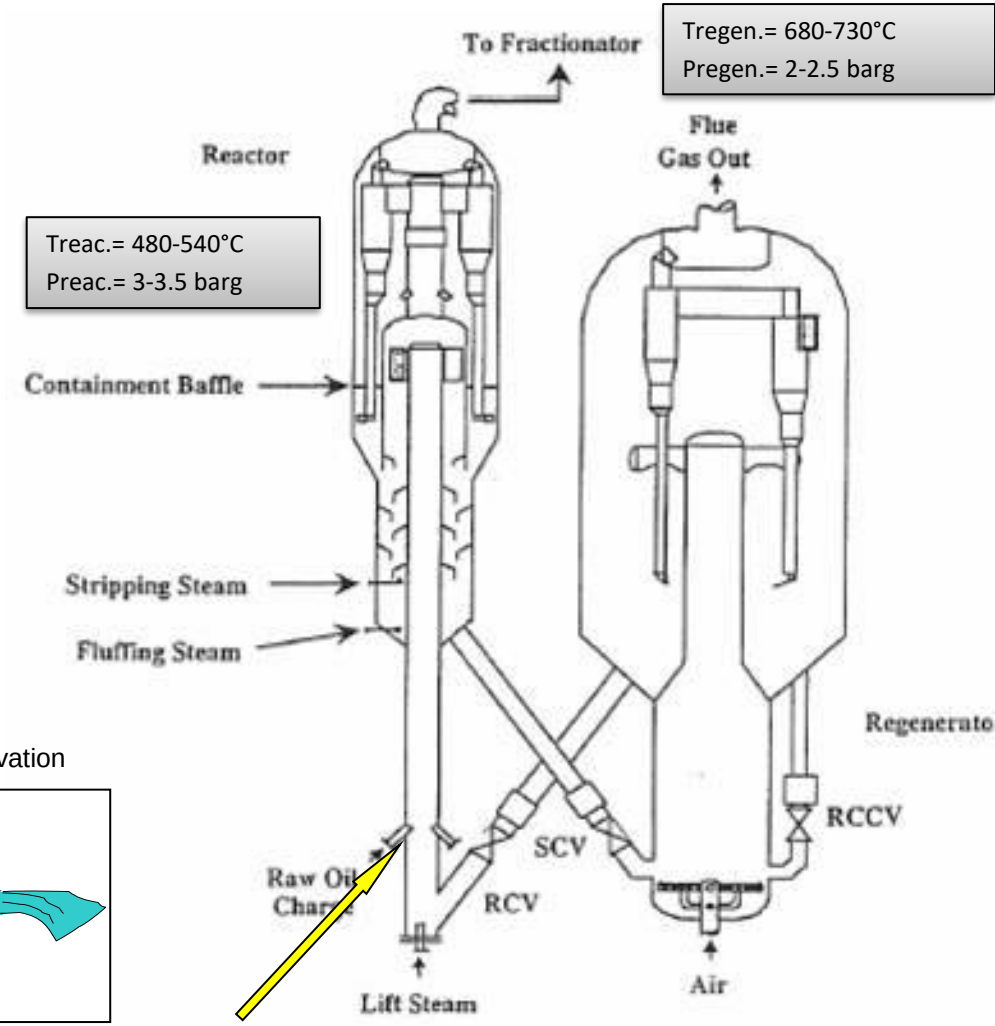
Houdry fix-bed



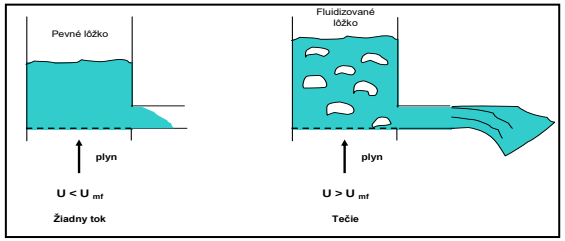
Fluid bed

Tregen.= 680-730°C
Pregen.= 2-2.5 barg

Treac.= 480-540°C
Preac.= 3-3.5 barg



Fluid bed – continuous catalyst re-activation

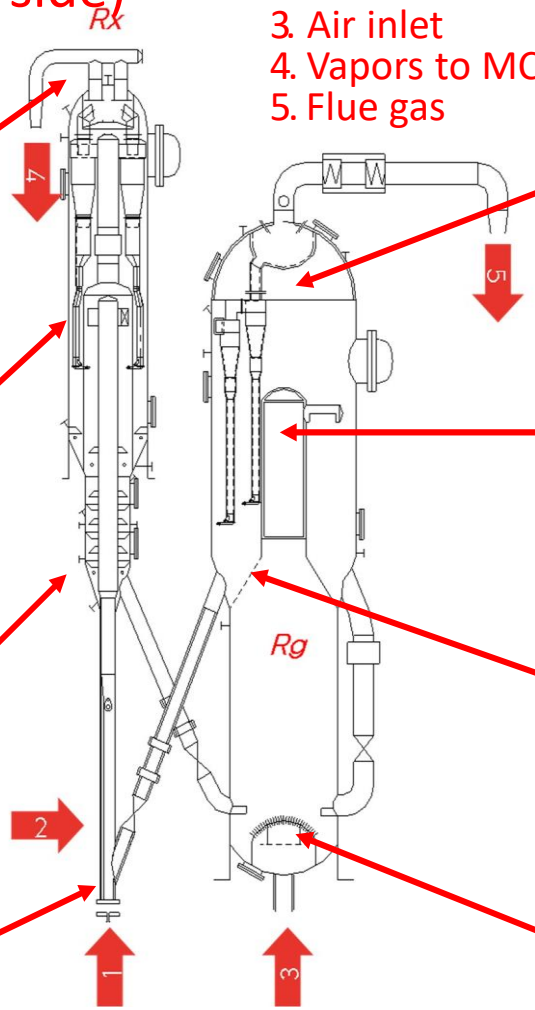


Reactions take place in the riser

CONVERSION TECHNOLOGIES / FCC

Process (UOP side by side)

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

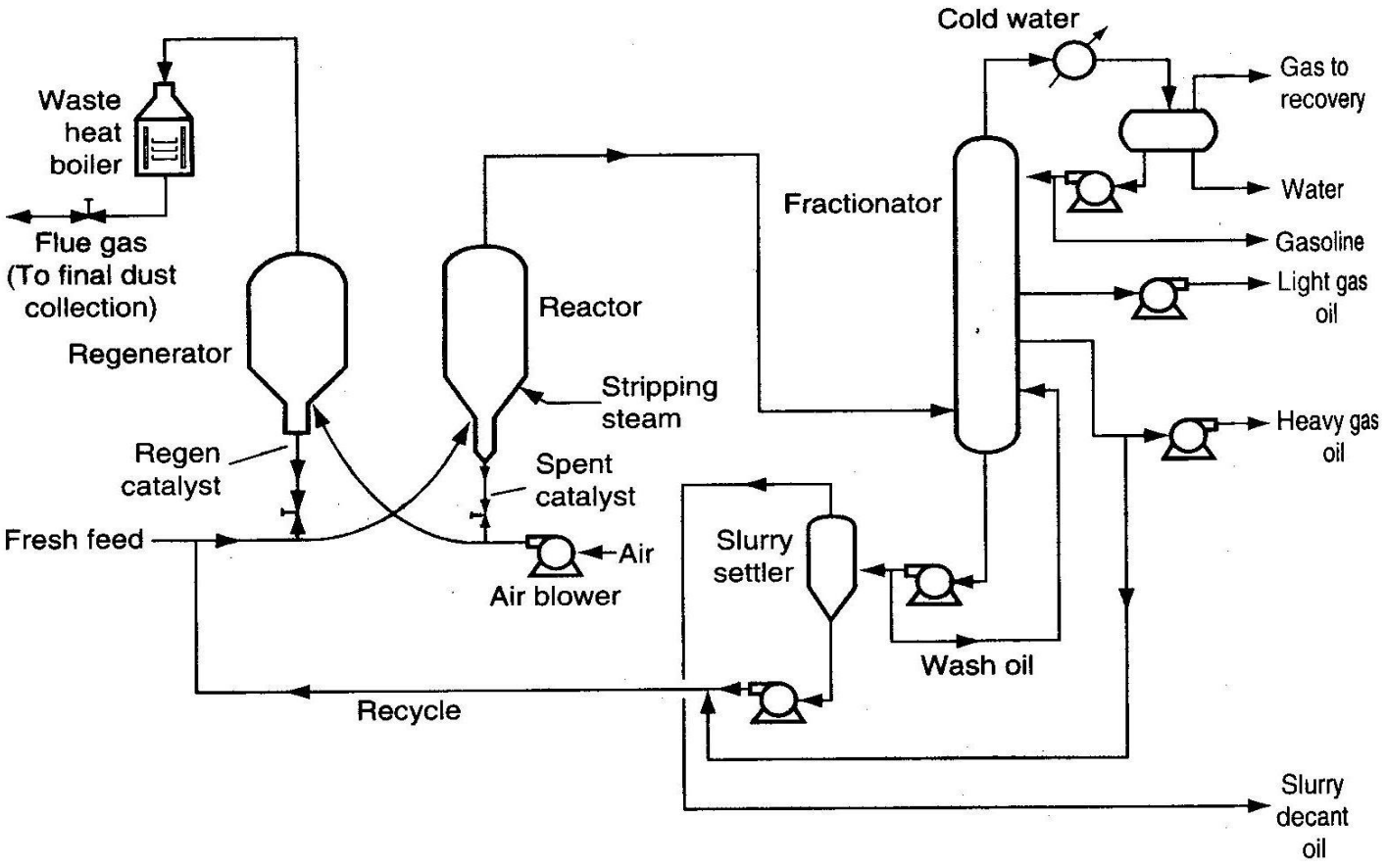


CONVERSION TECHNOLOGIES / FCC - CYCLONES

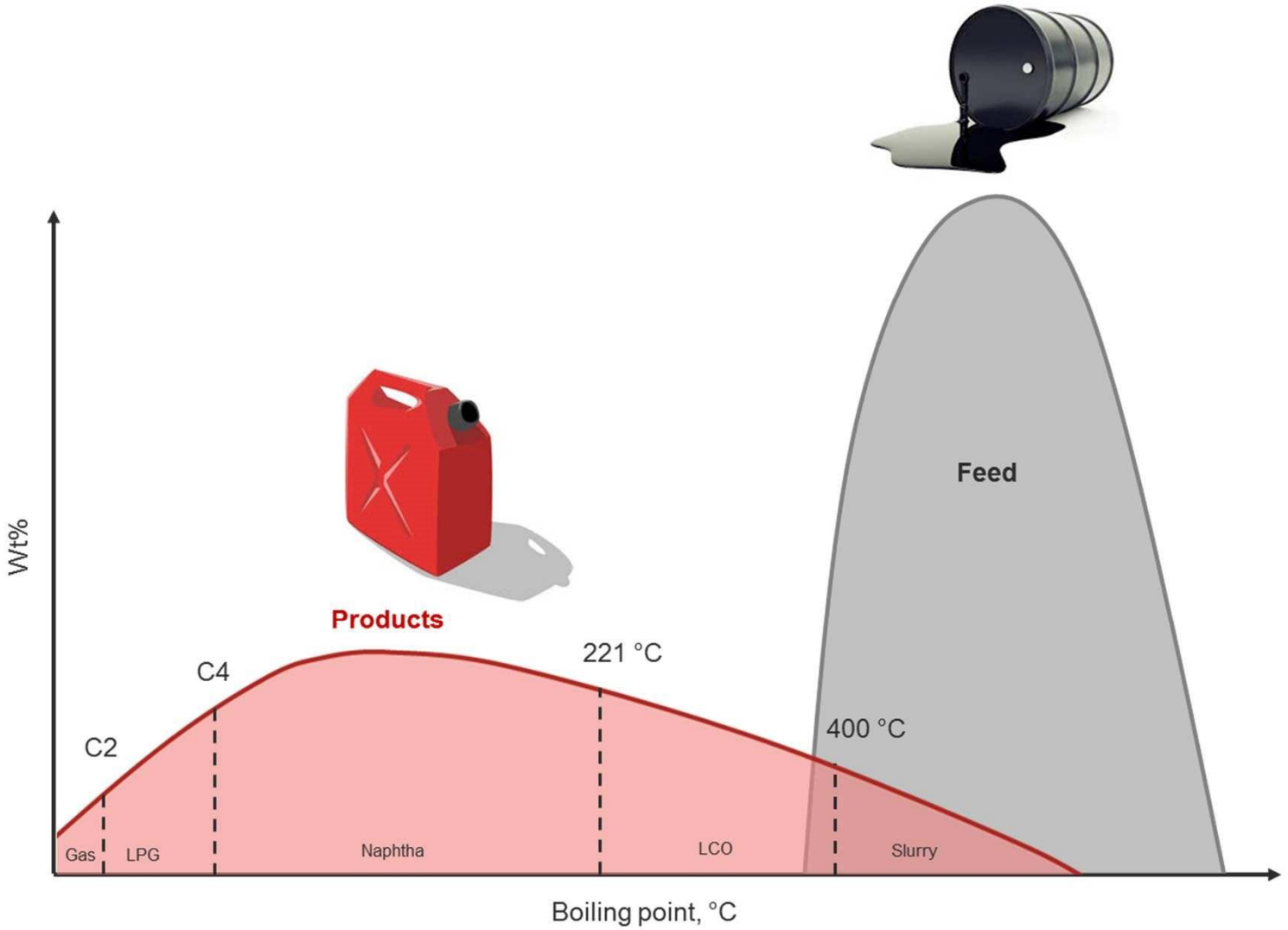
CONVERSION TECHNOLOGIES / FCC

Product yields:

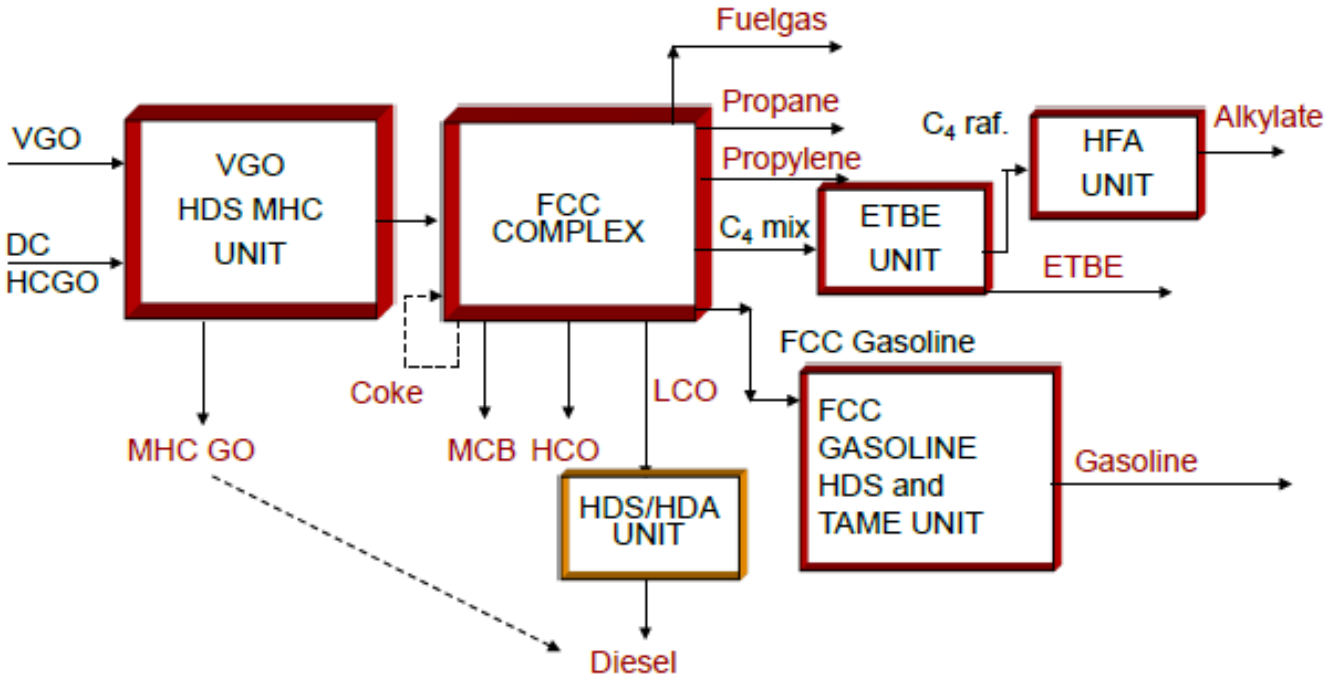
- Fuel gas 3-5 %
- C3-C4 fraction 7-20 %
- Naphtha 30-60 %
- LCO+HCO 11-20 %
- Reidue 10 -15%



TYPICAL PRODUCT QUALITIES



MOL DANUBE REFINERY/ FCC BLOCK



FCC Gasoline, Alkylate, ETBE: to MOGAS pool

LCO: Light Cycle Oil, to Diesel pool

HCO: Heavy Cycle Oil, to Fuel Oil pool

MCB: Main Column Bottom, to Fuel Oil pool or Carbon Black production

MOL DANUBE REFINERY/ FCC BLOCK

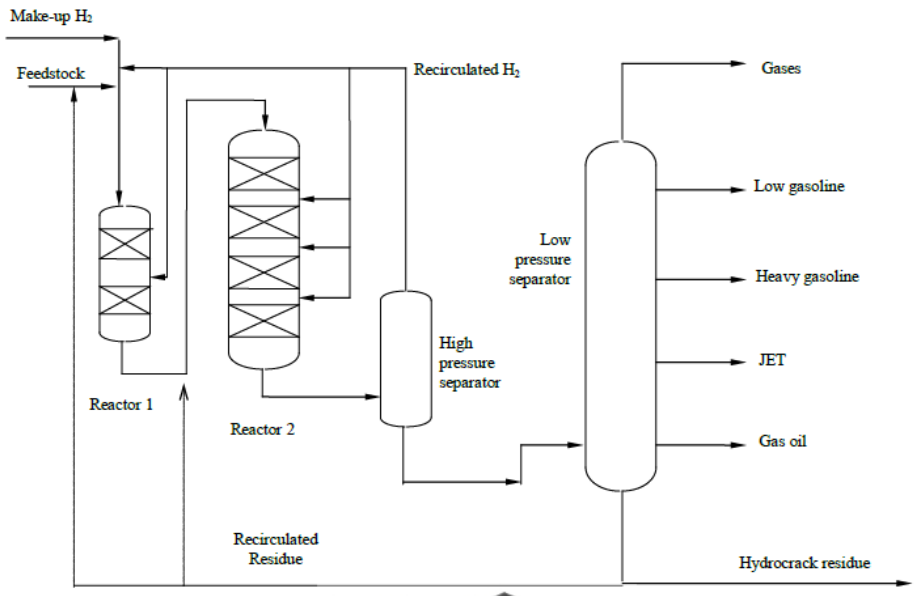
CONVERSION TECHNOLOGIES / HYDROCRACK

- **HYDROCRACKING: HYDROGEN+CRACKING**
- **MAIN REACTION: CRACKING LARGE HYDROCARBON MOLECULES IN THE PRESENCE OF HYDROGEN**
- **ONE OF THE OLDEST TECHNOLOGY**
  - 1915: first experiments
  - 1927: first industrial technology for brown coal hydrogentation (Bergius-LEUNA/Németország
  - 1925: technology for heavy distillate cracking
  - 1960: first commercial size hydrocracker in USA (Standard Oil)

CONVERSION TECHNOLOGIES / HYDROCRACK

HYDROCRACKING

Scheme of an one-stage hydrocracker with two reactor



Purpose: Breaking (cracking) large molecules in the feed into smaller ones in hydrogen atmosphere (increase white product yields)

Feed: vacuum gasoil, vacuum residue

Products: naphtha, gasoil components

Parameters:

Temperature: 300 - 450 °C

Pressure: 70 – 250 barg

Catalyst: Co/Mo/Pd/Pt – SiO_2/Al_2O_3

HDT AND HCK CATALYSTS

HCK catalysts

A
(cra
metals
g function)

amorf
SiO_2-Al_2O_3,
Al_2O_3,
x-Al_2O_3
(x=halogen)

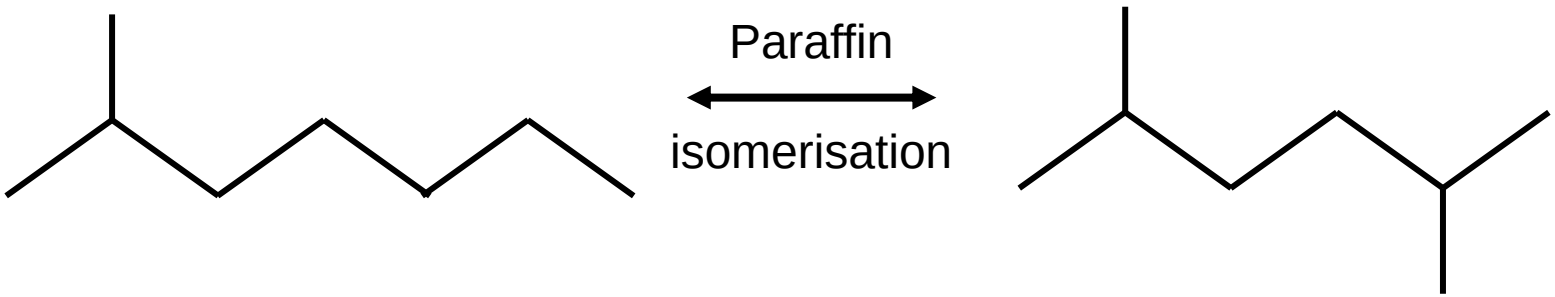
z VIA gr. (Mo, W)
+ VIIIA gr. (Co, Ni)

Large active suface is needed for the efficient operation of both functions

HDT AND HCK REACTIONS

Main reactions

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



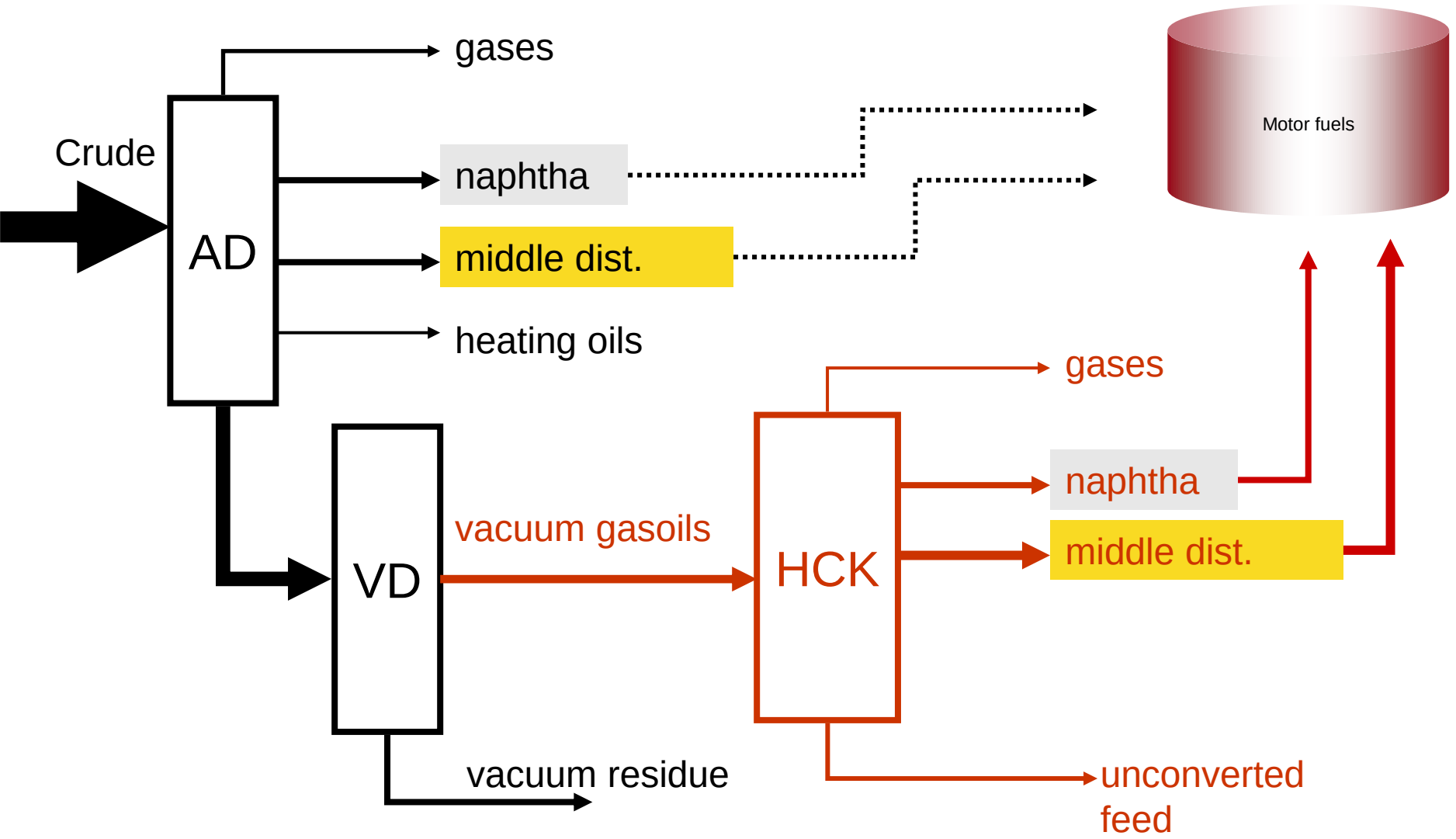
Other reactions

Hydro-decyclisation

Hydrogenation of aromatics

Hydro-dealkylation

VACUUM GASOIL (VGO) HYDROCRACKING



PROPERTIES OF VGO

Typical value for REB Crude

Analysis, UOM	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

- Nitrogen containing molecules are catalyst poisons

- Heavy metals as well

V, Ni, Fe, Na, Cu, Pb, As

SIMPLIFIED PROCESS FLOW (REACTOR SECTION)

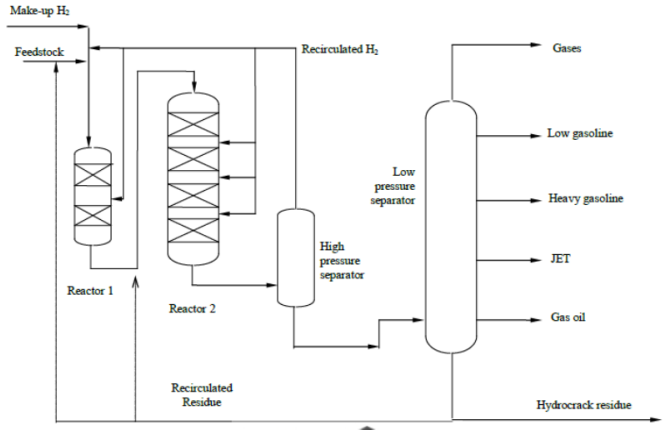
VARIOUS HCK SCHEMES

ONE STEP "ONCE THRU"
NO RECIRCULATION, SIMPLE, BASE OIL PRODUCTION

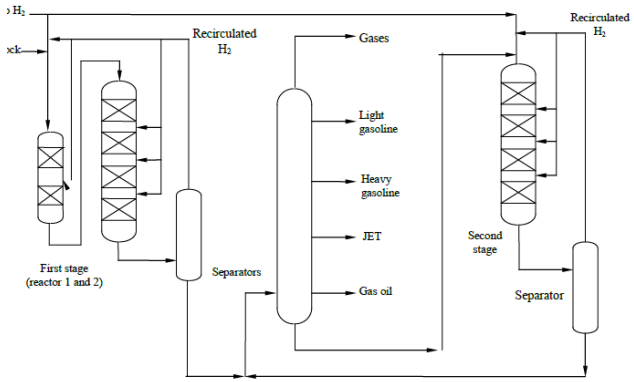
ONE STEP WITH UCO (UNCONVERTED OIL) RECIRCULATION
MAIN FRACTIONATOR BOTTOM PRODUCT RECIRCULATION
HIGHER DISTILLATE YIELDS,
CONVERSION ~ 30-60%
HIGH ENERGY CONSUMPTION

TWO STEP WITH UCO RECIRCULATION
SEPARATION OF REACTION STEPS,
COMPLEX SETUP
HIGH INVESTMENT COSTS
CONVERSION: ~ 100%
HIGH ENERGY CONSUMPTION

Scheme of an one-stage hydrocracker with two reactor

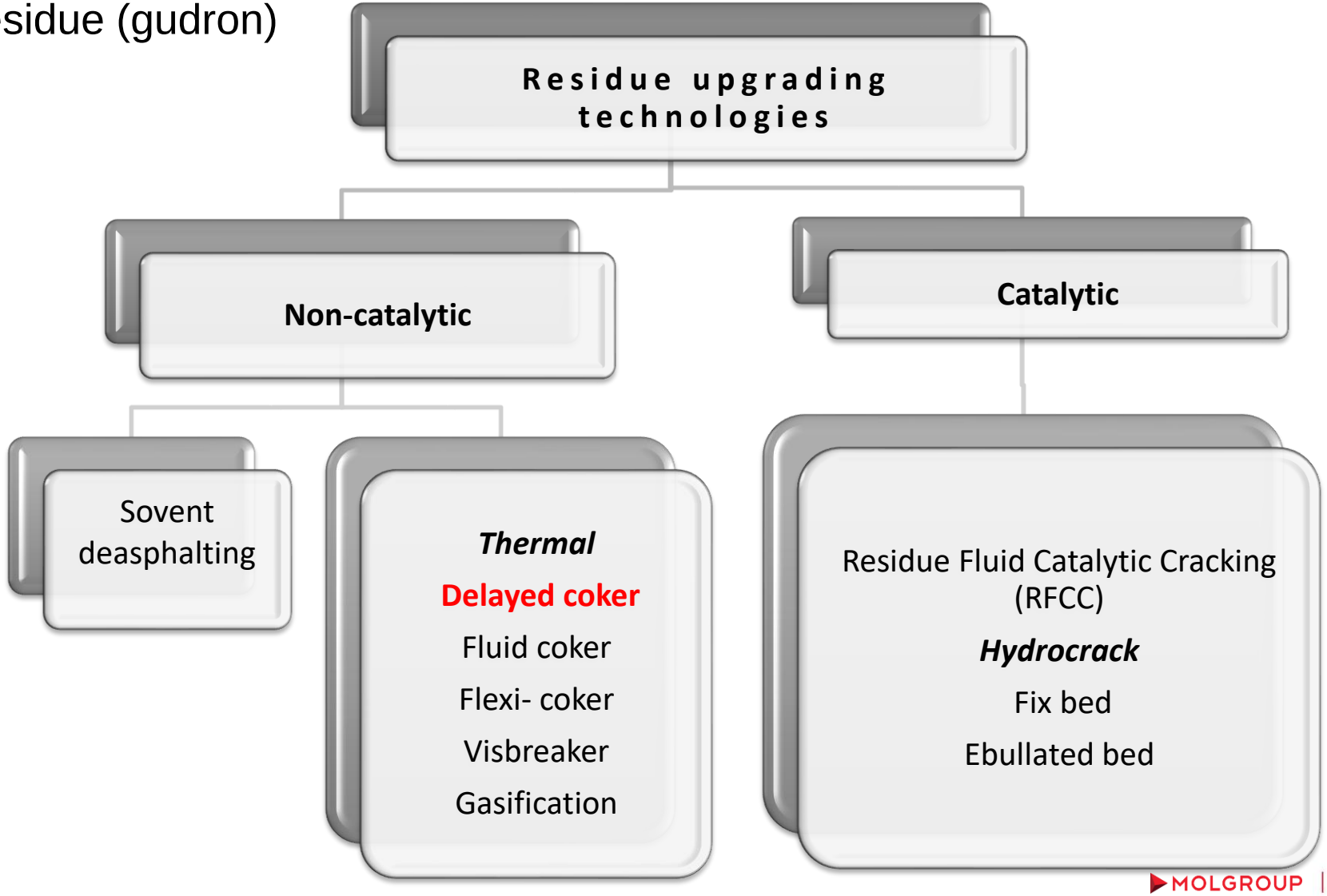


Scheme of an two-stage hydrocracker

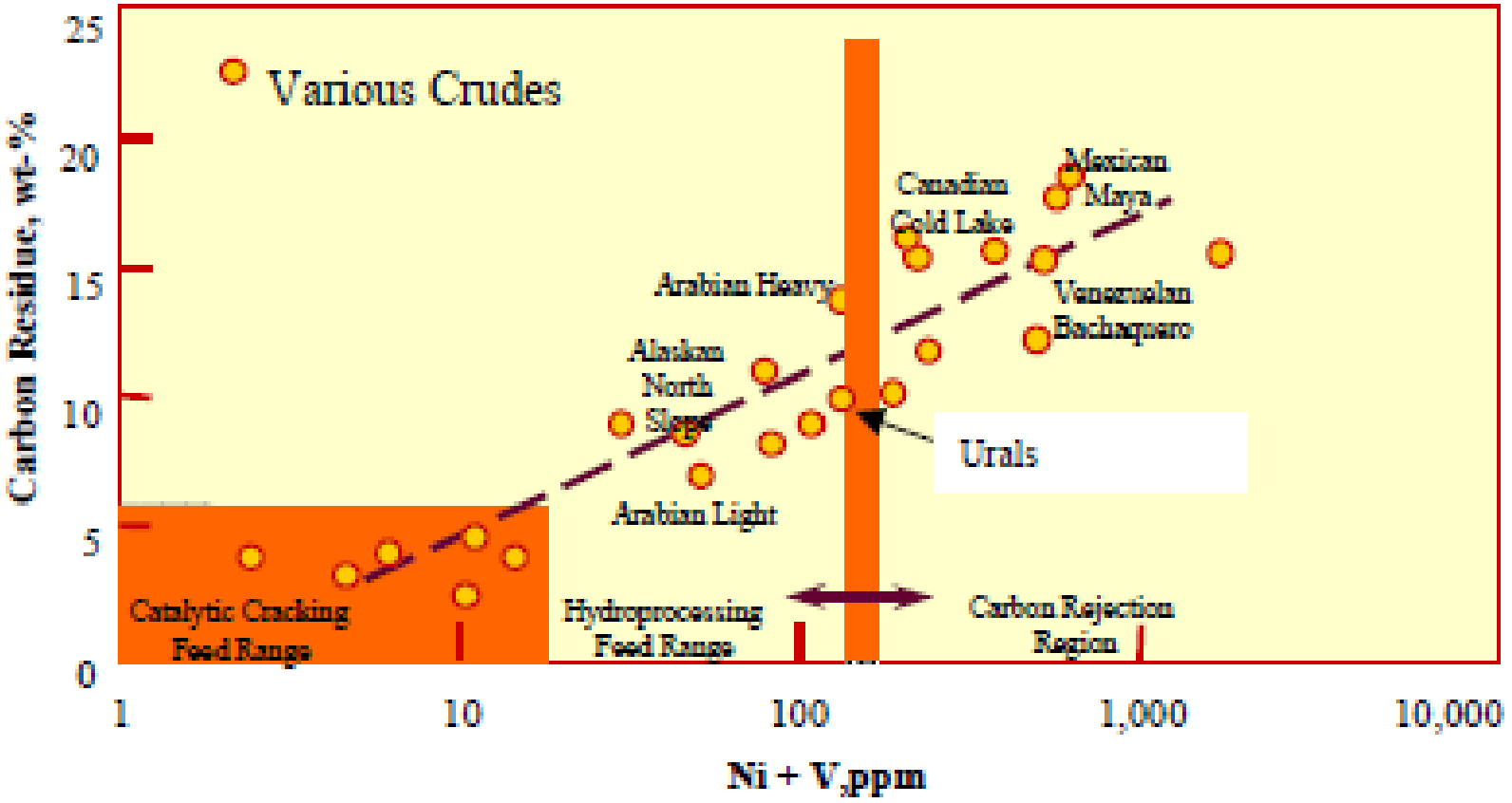


RESIDUE UPGRADING

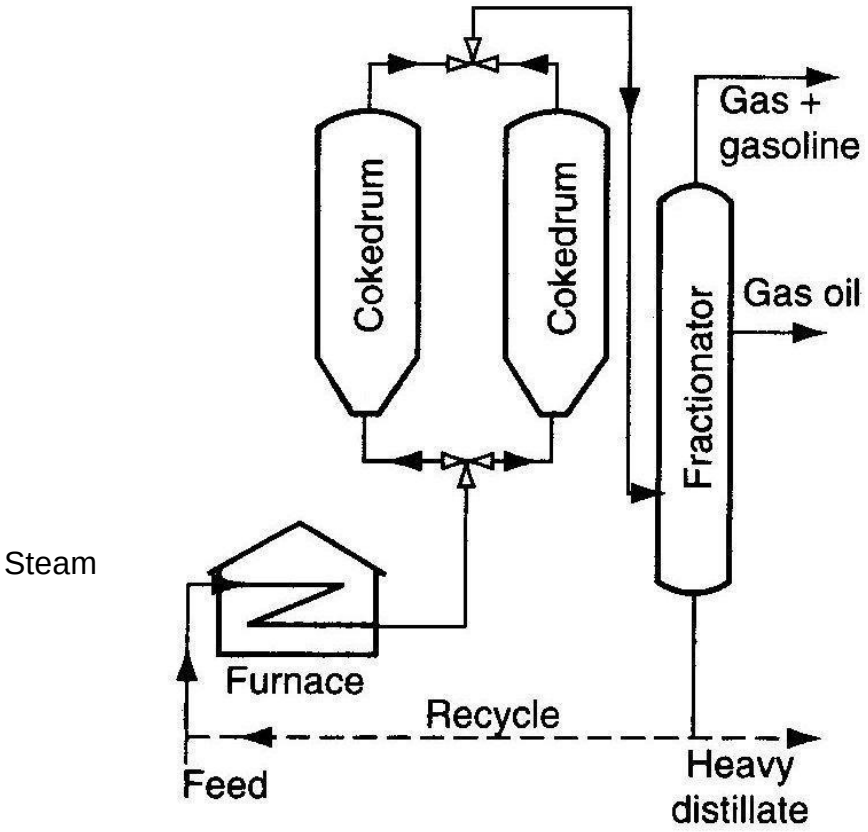
Feed: vacuum residue (gudron)



CARBON REJECTION OR HYDROGEN INPUT



RESIDUE UPGRADING / DELAYED COKING



Thermal cracking process

Purpose: produce valuable products (need de-sulphurisation) while heavy components are converted to solid coke

Feed: vac. residue (gudron)

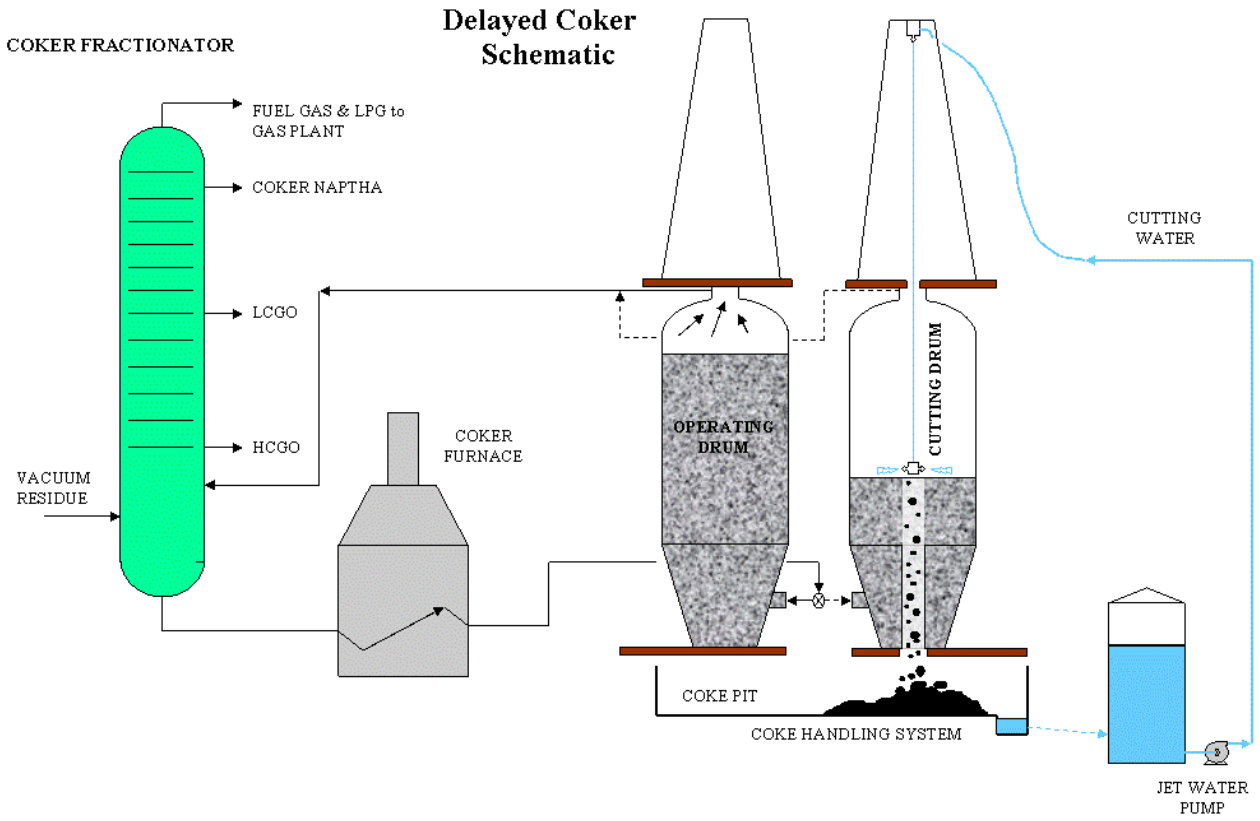
Products: gases, naphtha, gasoil, petcoke

Parameters:

Temperature: 480 - 520 °C

Pressure: 1 – 5 barg

RESIDUE UPGRADING / DELAYED COKING



RESIDUE UPGRADING / DELAYED COKING

RESIDUE UPGRADING / DELAYED COKING

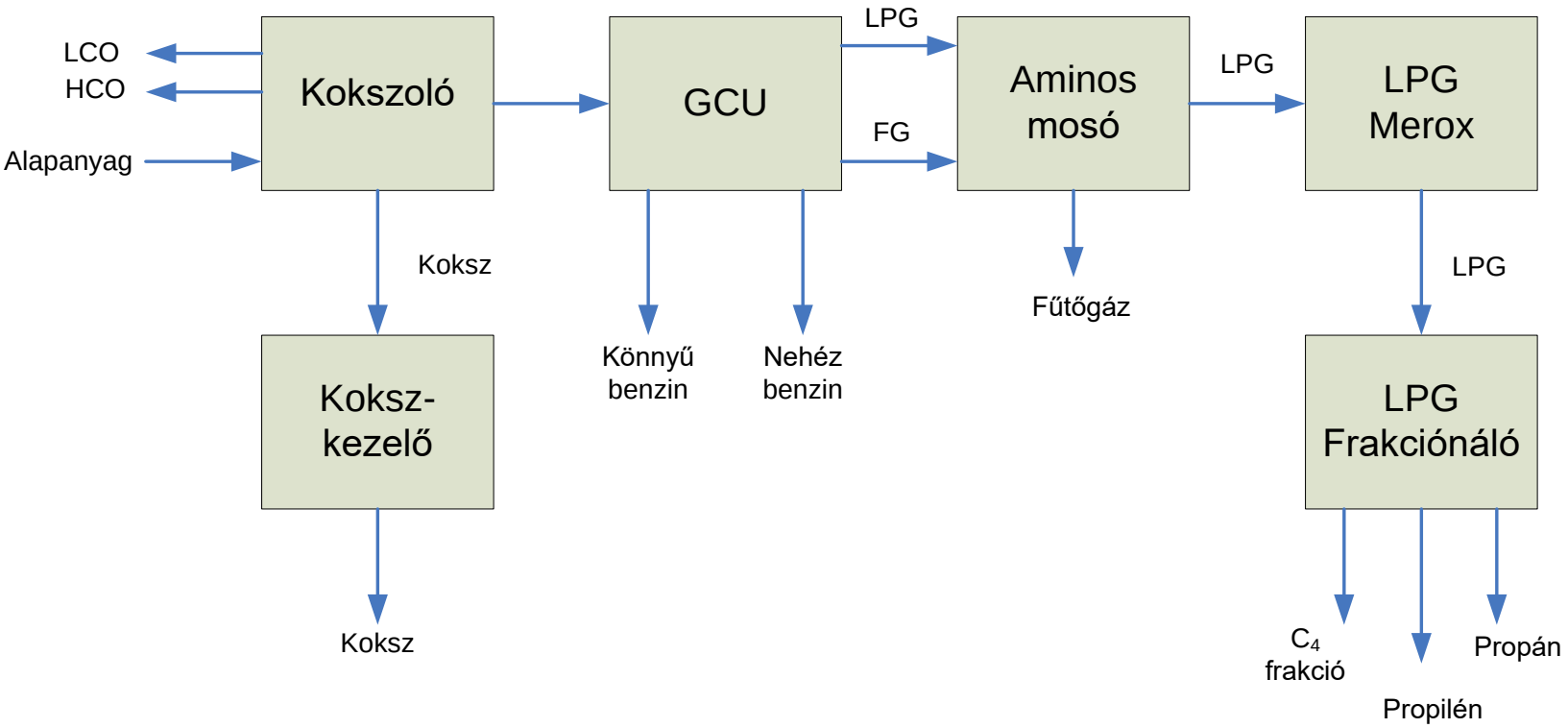
AS A RESULT OF COMPLEX REACTIONS, HEAVIEST COMPONENTS OF THE FEED ARE CONVERTED TO SOLID COKE, WHILE MAJORITY OF THE FEED IS CONVERTED TO VALUABLE, LOWER BOILING POINT PRODUCTS

COKING PROCESS IS SO COMPLEX, IT CANNOT BE DESCRIBED BY EXACT REACTIONS BUT IT CONSISTS OF THREE SEPARATE STEPS:

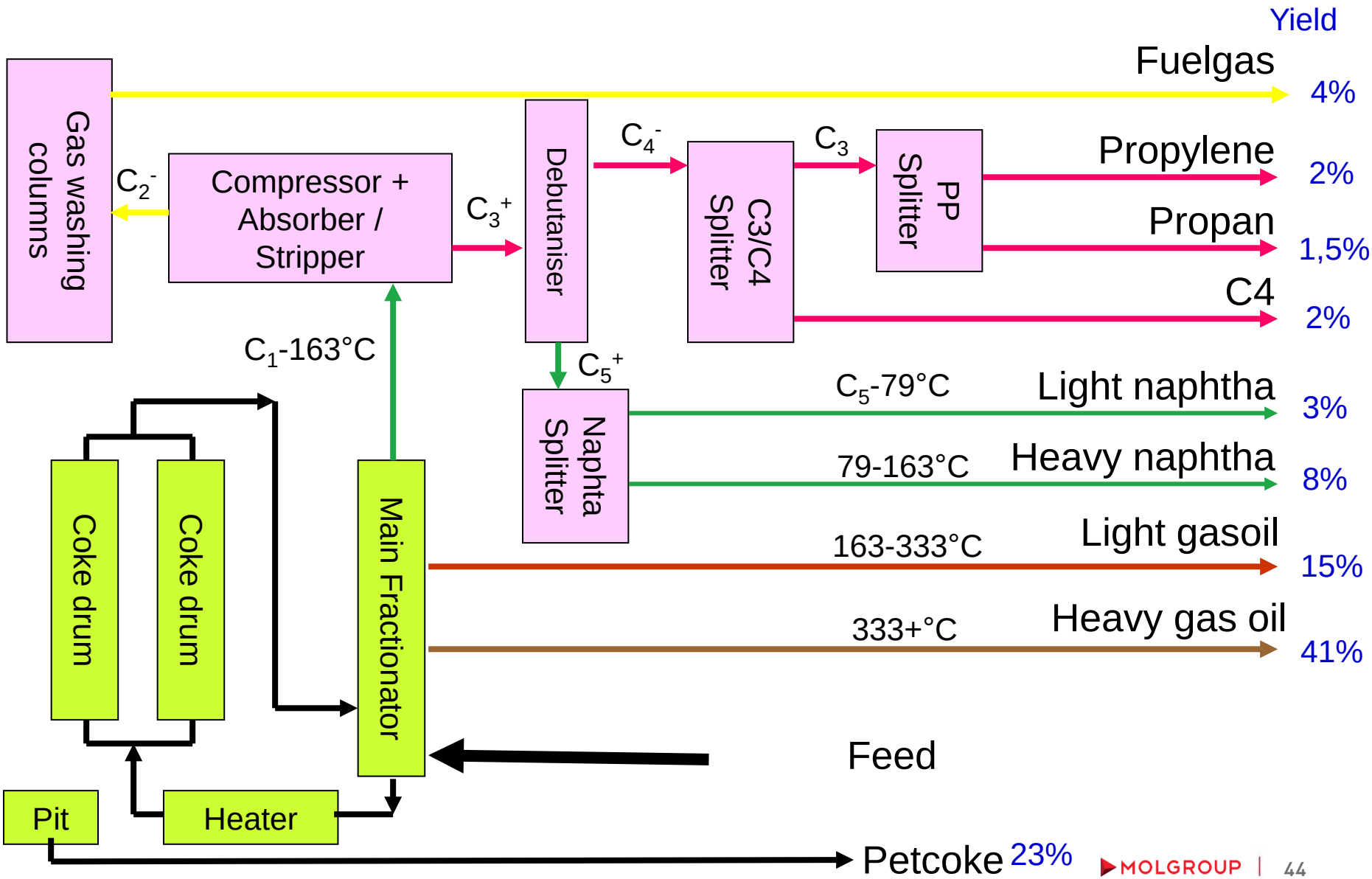
- Evaporation and mild cracking of the feed in the tubes of the feed heater;
- Further cracking of hydrocarbon vapours in the coke drums;
- Polymerisation and cracking of liquid phase in the coke drum to gases and coke.

PRODUCT YIELDS AND QUALITIES ARE BASICALLY DEFINED BY THREE PARAMETERS : TEMPERATURE, PRESSURE AND RECIRCULATION RATIO.

RESIDUE UPGRADING / DELAYED COKING

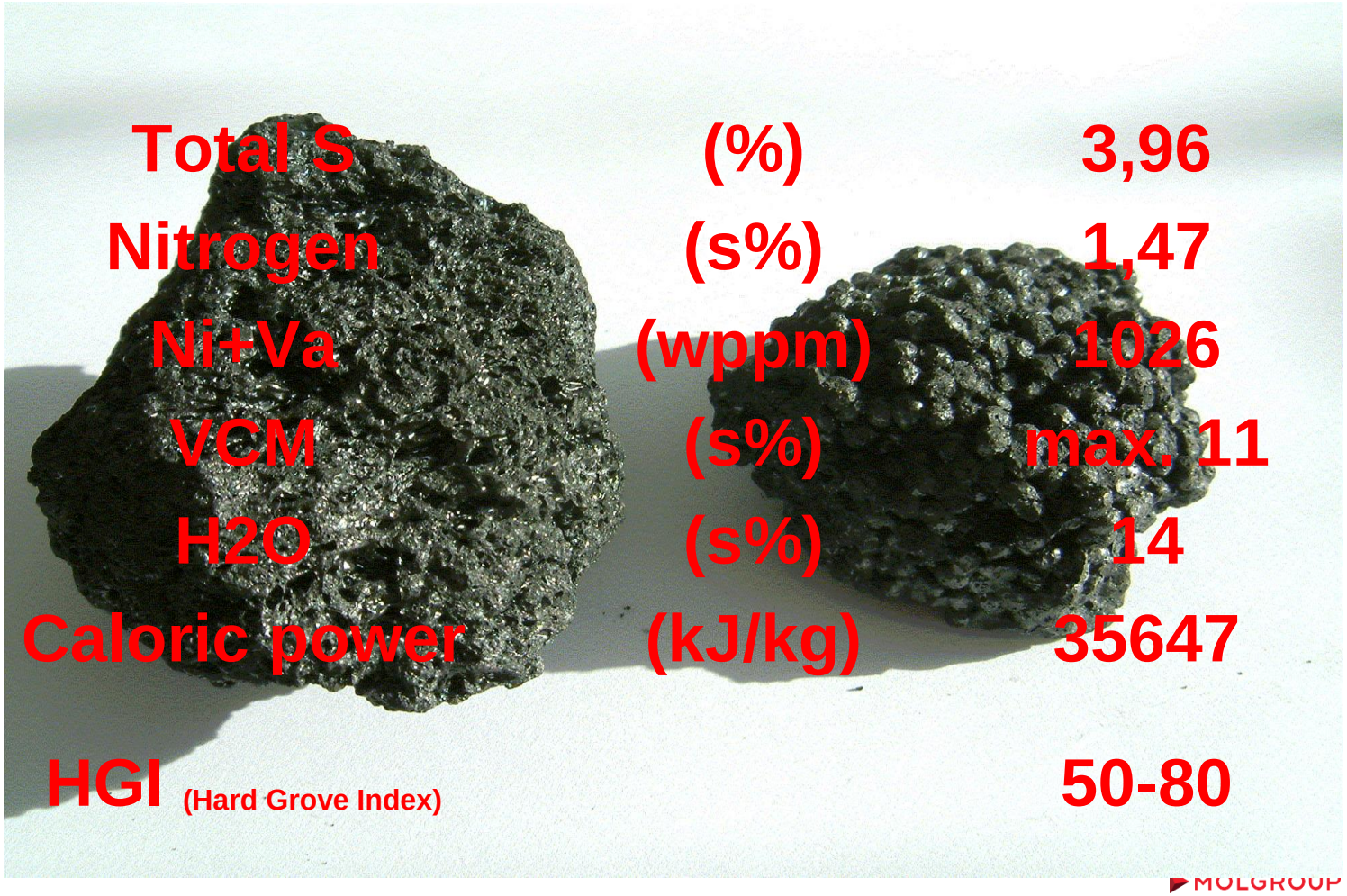


RESIDUE UPGRADING / DELAYED COKING



RESIDUE UPGRADING / DELAYED COKING

Petcoke properties



Total S	(%)	3,96
Nitrogen	(s%)	1,47
Ni+Va	(wppm)	1026
VCM	(s%)	max. 11
H2O	(s%)	14
Caloric power	(kJ/kg)	35647
HGI (Hard Grove Index)		50-80

DANUB EREFINERY – DELAYED COKER

THANK YOU FOR YOUR ATTENTION!

MOLGROUP