Syncrude upgrading

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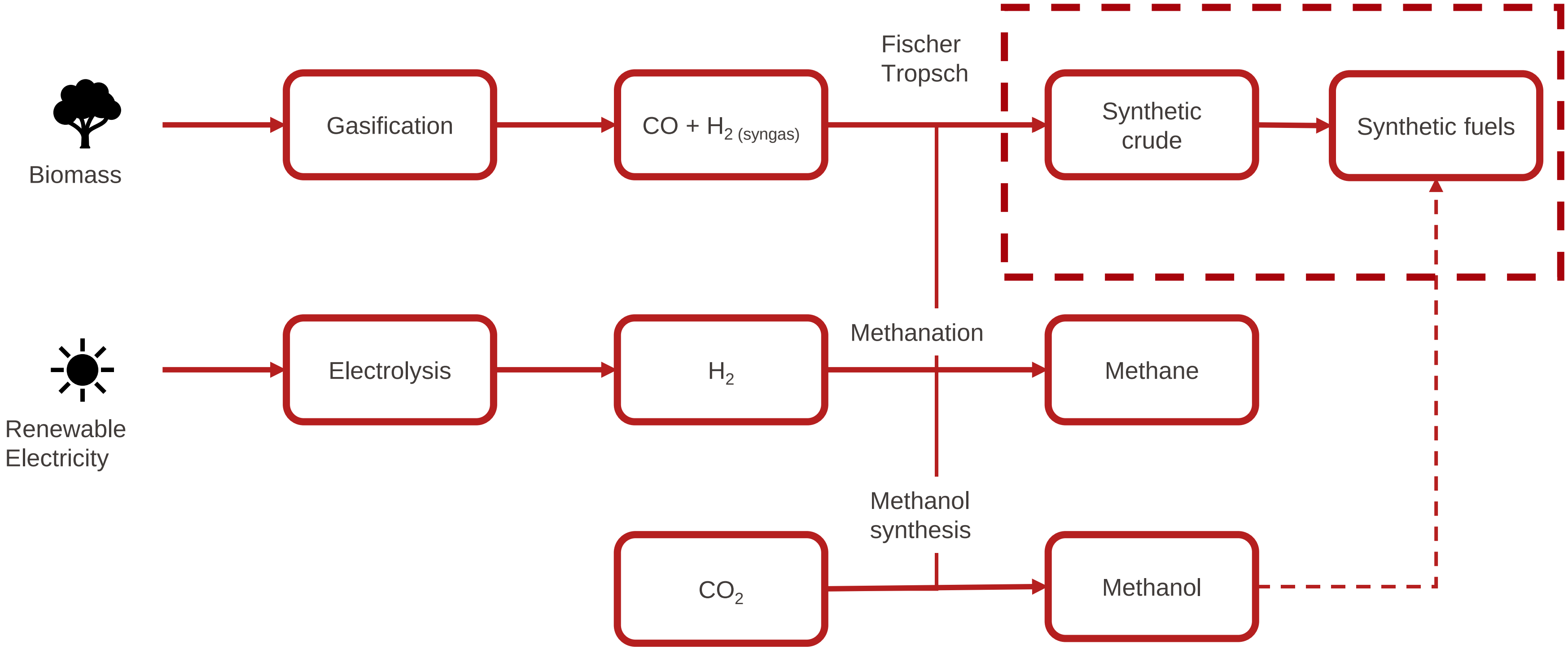
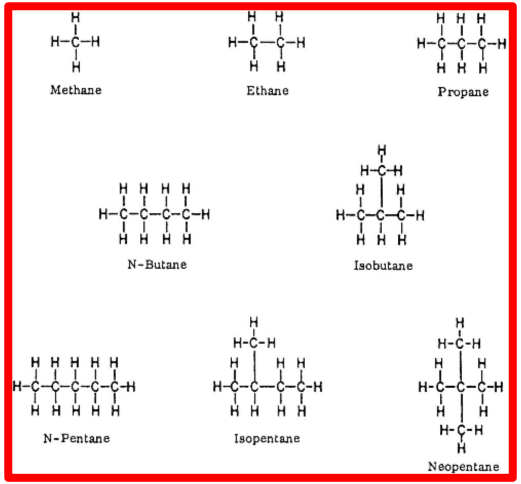
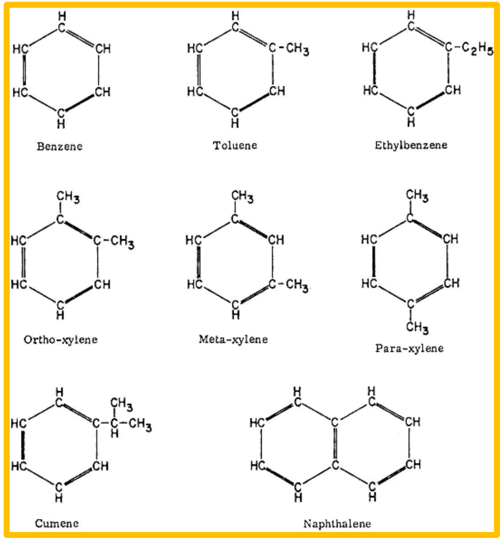
Processes for renewable fuels production



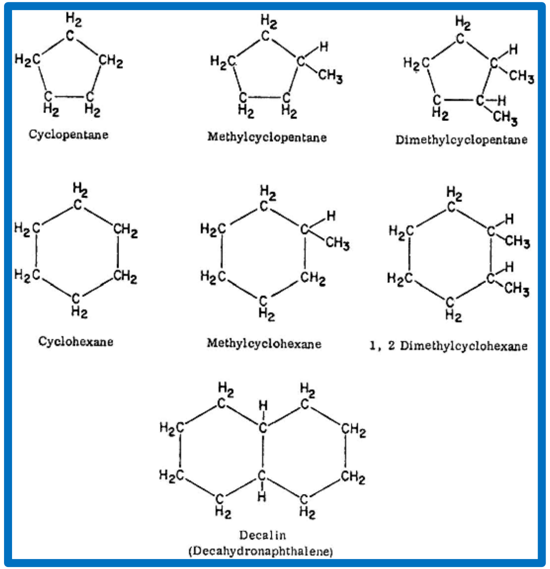
(Syn)crude oil components



Paraffines

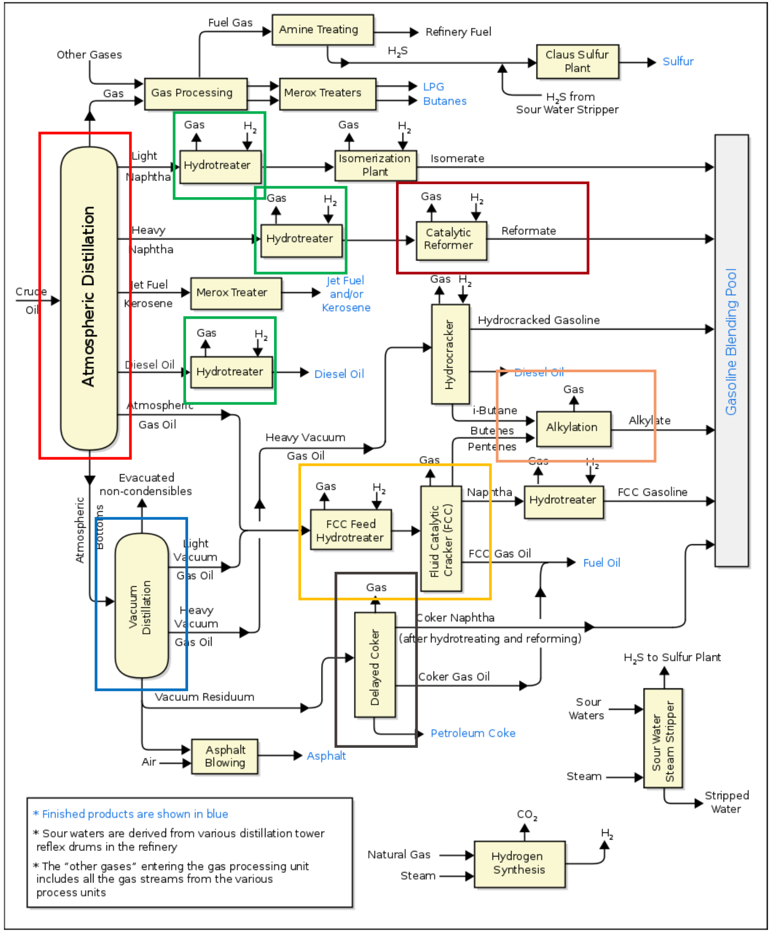


Aromatics



Naphthenes

(Syn)crude value chain



* Finished products are shown in blue

* Sour waters are derived from various distillation tower reflex drums in the refinery

* The "other gases" entering the gas processing unit includes all the gas streams from the various process units

🟥 First distillation (topping)

🟦 Second distillation (vacuum)

🟩 Hydro-treatment

⬛ Coking

🟨 Fluid catalytic cracking

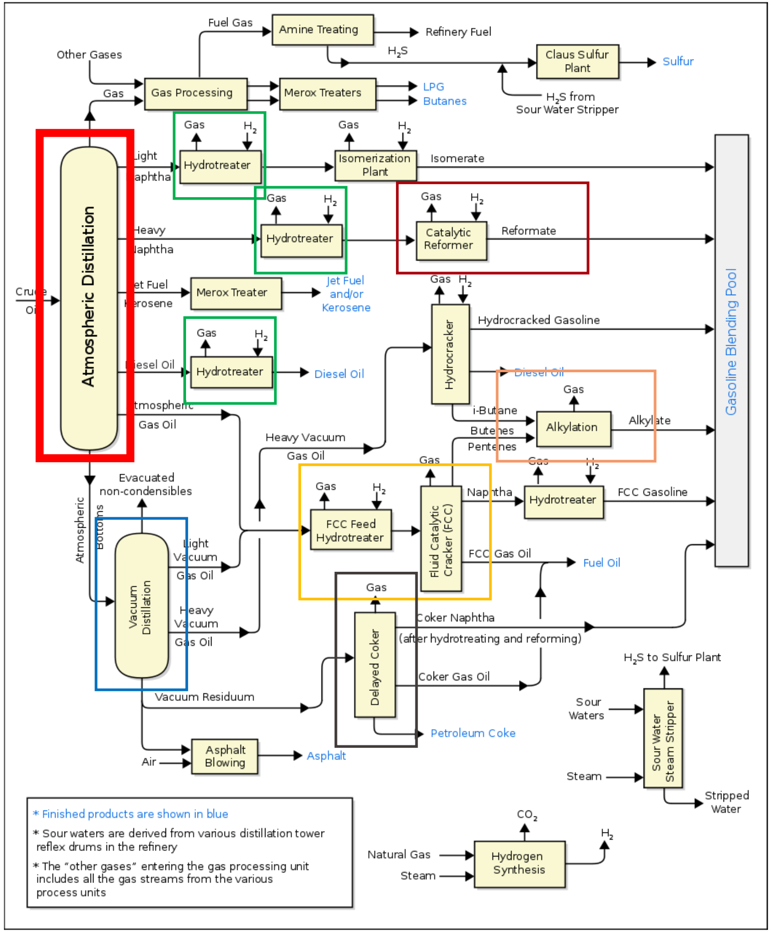
🟥 Reforming

🟧 Alkylation

Nomenclature

Distillate fraction	Boilingpoint (°C)	C-atom/molecule
▪ Gases	<30	C1-C4
▪ Gasoline	30 –210	C5-C12
▪ Naphtha	100 –200	C8-C12
▪ Kerosene	150 –250	C11-C13
▪ Diesel, Fuel oil	140 –400	C13-C17
▪ Atmospheric Gasoil	220 –345	C20-C45
▪ Heavy Fuel oil	315–540	C20-C45
▪ Atmospheric residue	> 540	>C30
▪ Vacuum residue	> 615	>C60

(Syn)crude value chain



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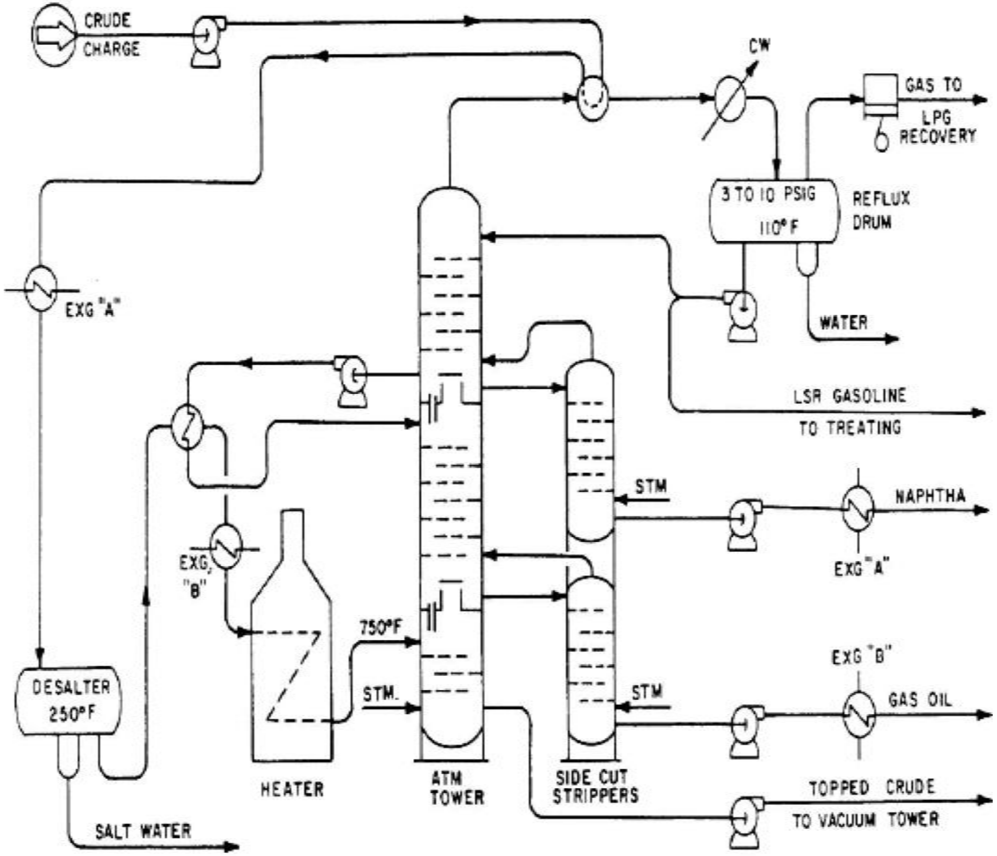
First distillation column



LPG

Gasoline

Naphta

Diesel

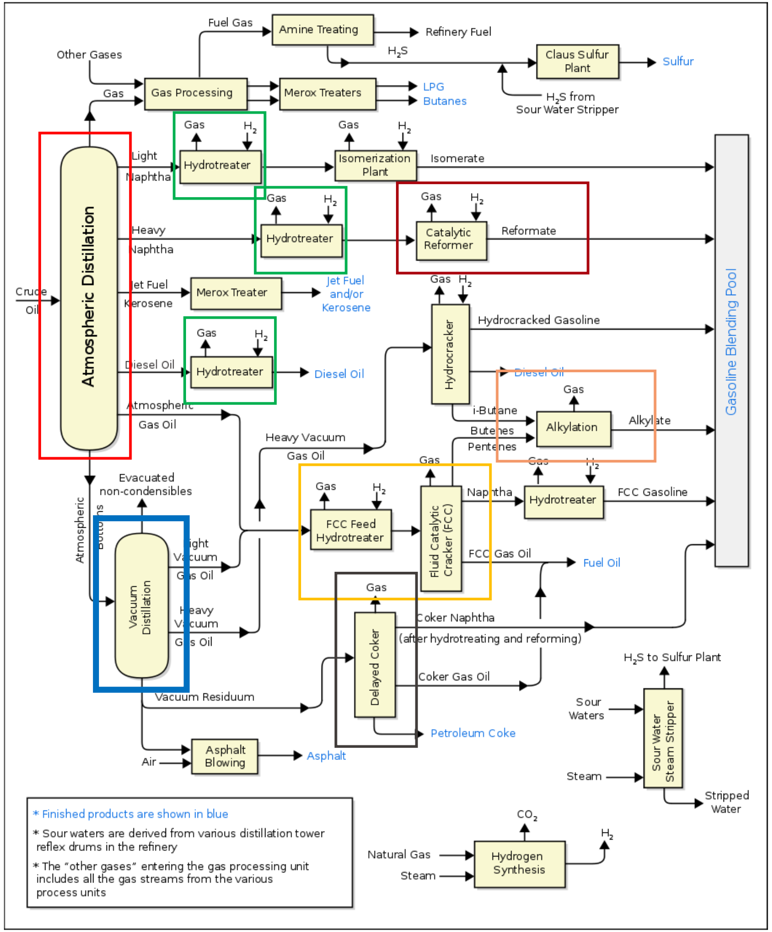
Vacuum residual

Low value

High value

Low value

(Syn)crude value chain



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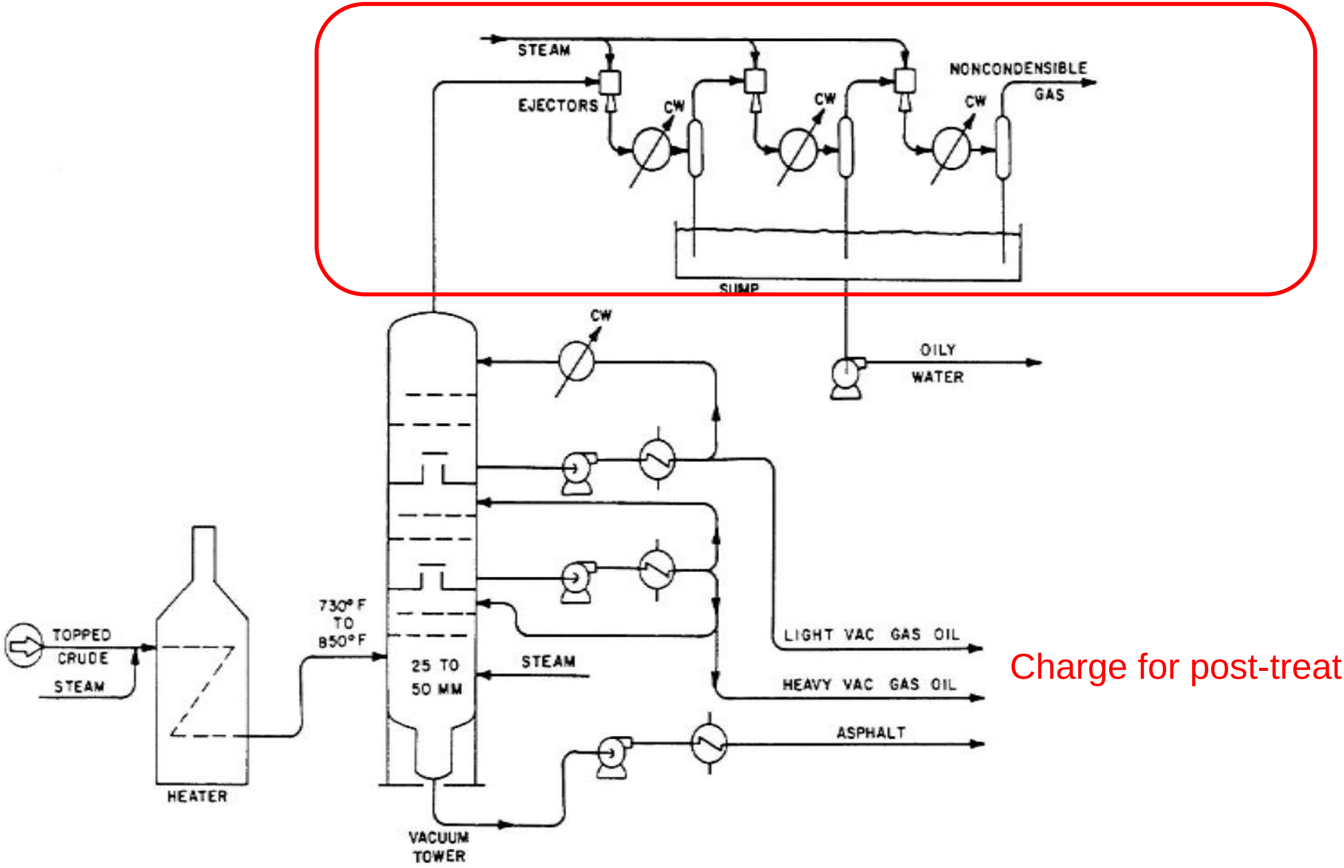
🟧	Alkylation

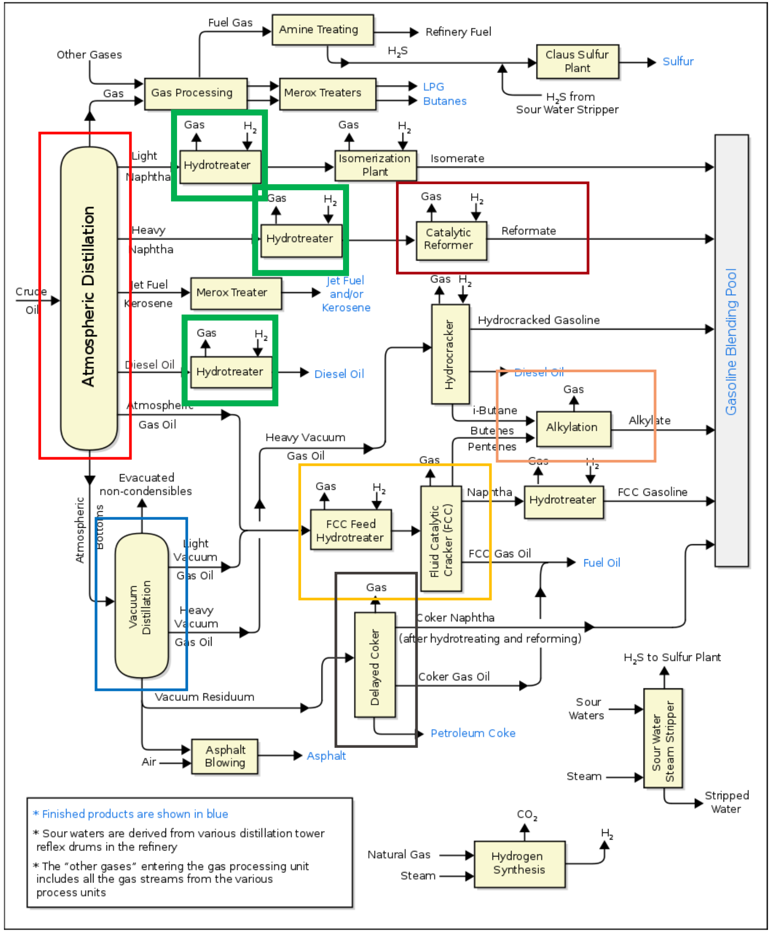
Vacuum distillation



Ejectors to keep vacuum conditions

Charge for post-treatment

(Syn)crude value chain



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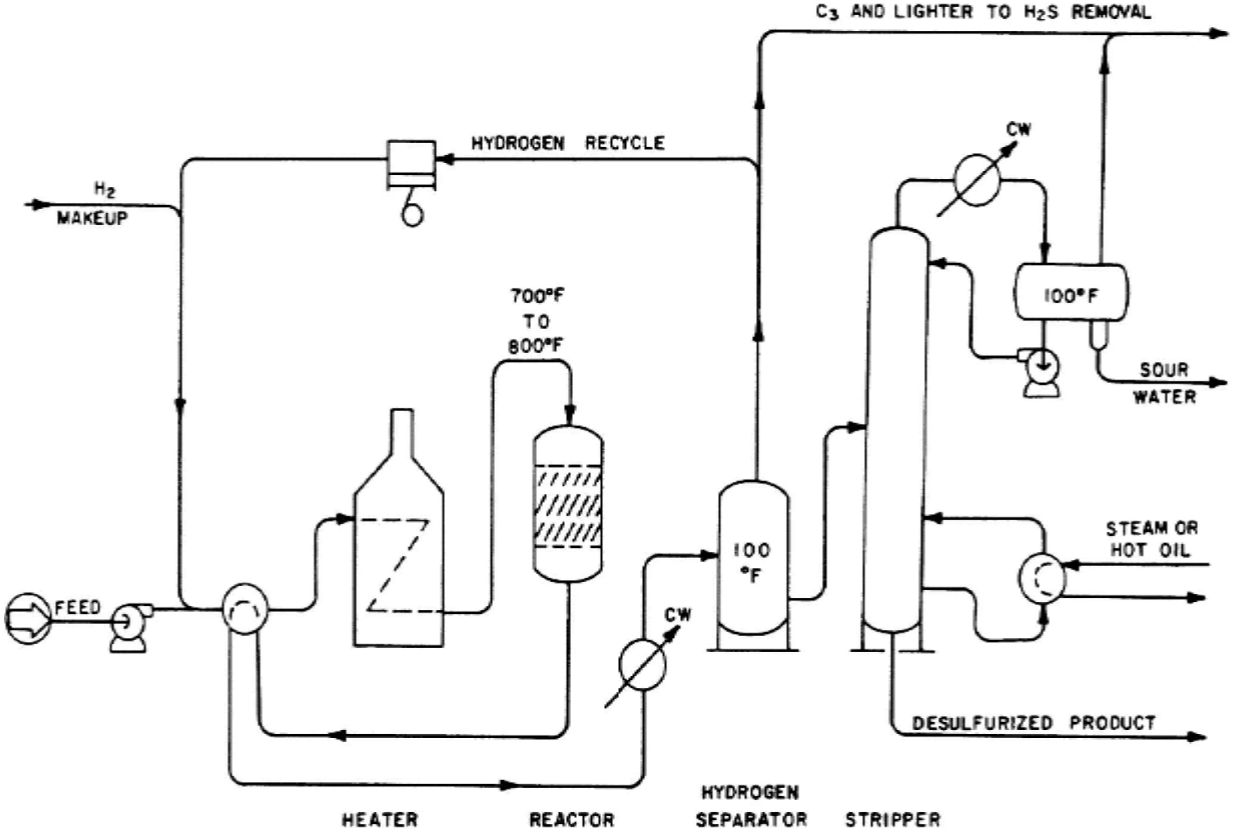
Hydrotreating

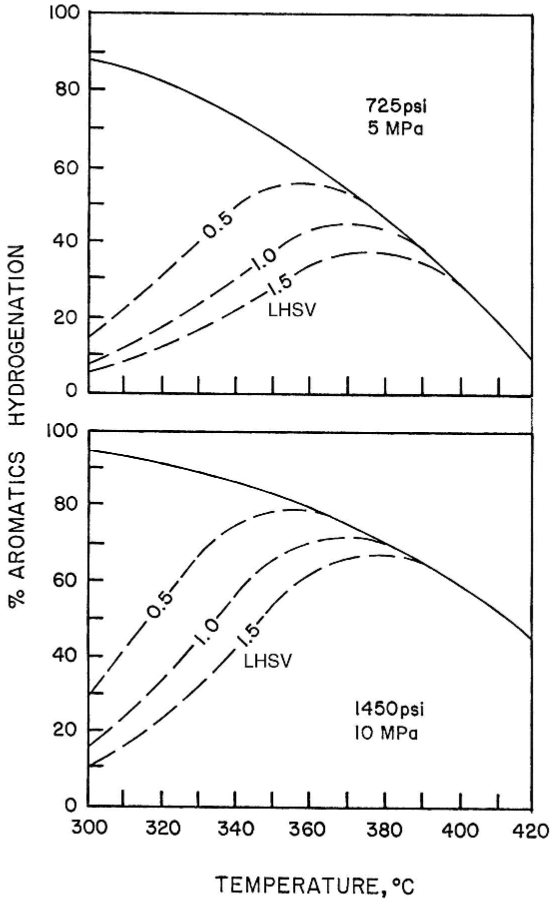
- Prior to catalytic processes, removal of:
  - Sulfur (RSH + H_2 → H_2S + RH)
  - Nitrogen (RNH + H_2 → NH_3 + RH)
  - Oxygen (ROH + H_2 → H_2O + RH)
  - Metals
- Saturation of unstable hydrocarbons & de-aromatization of kerosene
  - E.g.: $C_6H_6 + 6H_2 \rightarrow C_6H_{12}$

Catalyst	Hydro-desulphurization	Hydro-denitrogenation	Aromatics hydrogenation
Co-Mo/Al_2O_3	+++	+	o
Ni-Mo/Al_2O_3	++	++	+
Ni-W/Al_2O_3	+	+	+++

Example #1: desulfurisation

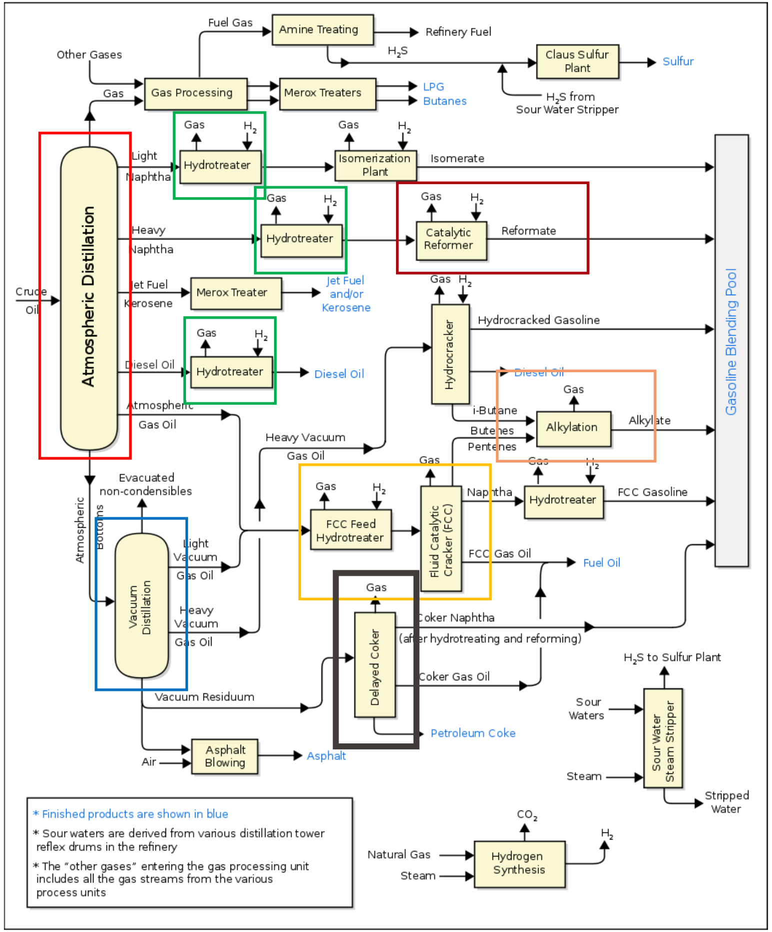


Example #2: Dearomatisation



- Operating point: compromise between thermodynamic equilibrium and reaction kinetics
- Effect of space velocity

(Syn)crude value chain



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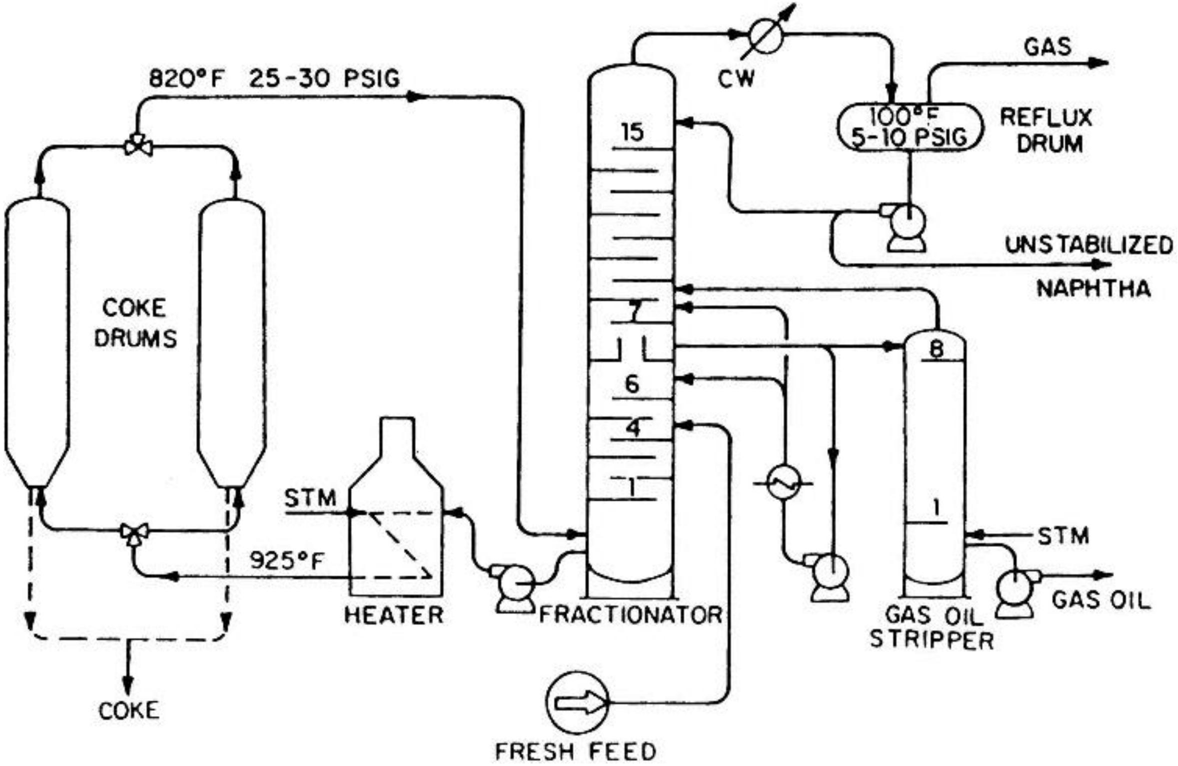
Coking #1


820°F 25-30 PSIG
COKE DRUMS
STM
925°F
HEATER
COKE
CW
GAS
100°F
5-10 PSIG
REFLUX DRUM
15
7
6
4
1
8
1
UNSTABILIZED NAPHTHA
STM
GAS OIL
FRACTIONATOR
GAS OIL STRIPPER
FRESH FEED

Coking #2

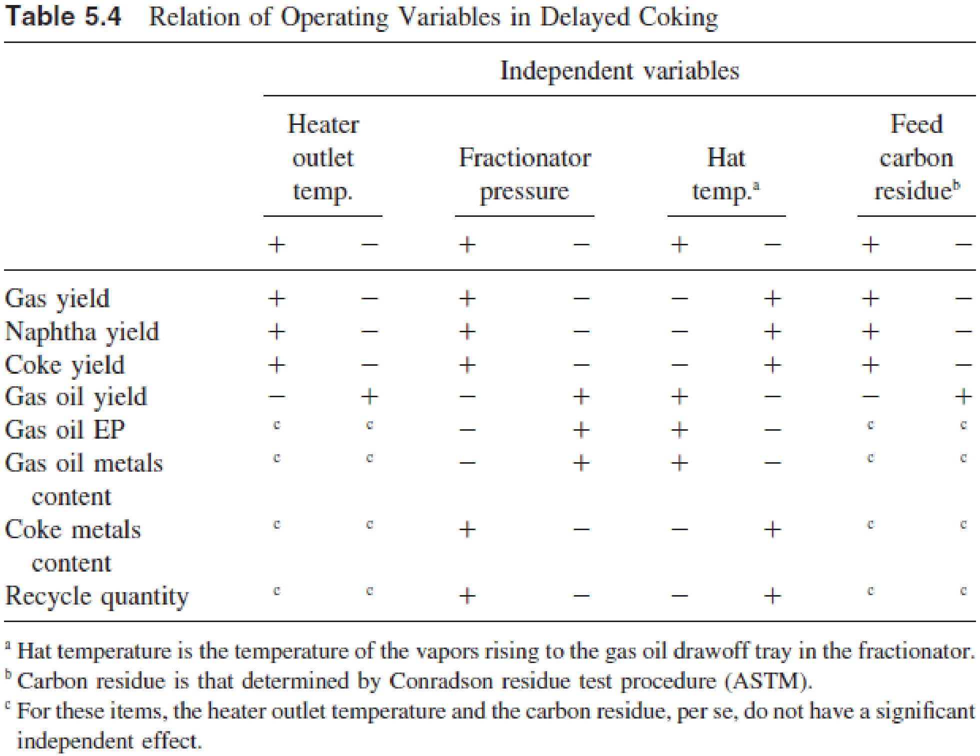


Table 5.4 Relation of Operating Variables in Delayed Coking

	Independent variables							
	Heater outlet temp.		Fractionator pressure		Hat temp.[a]		Feed carbon residue[b]	
	+	−	+	−	+	−	+	−
Gas yield	+	−	+	−	−	+	+	−
Naphtha yield	+	−	+	−	−	+	+	−
Coke yield	+	−	+	−	−	+	+	−
Gas oil yield	−	+	−	+	+	−	−	+
Gas oil EP	[c]	[c]	−	+	+	−	[c]	[c]
Gas oil metals content	[c]	[c]	−	+	+	−	[c]	[c]
Coke metals content	[c]	[c]	+	−	−	+	[c]	[c]
Recycle quantity	[c]	[c]	+	−	−	+	[c]	[c]

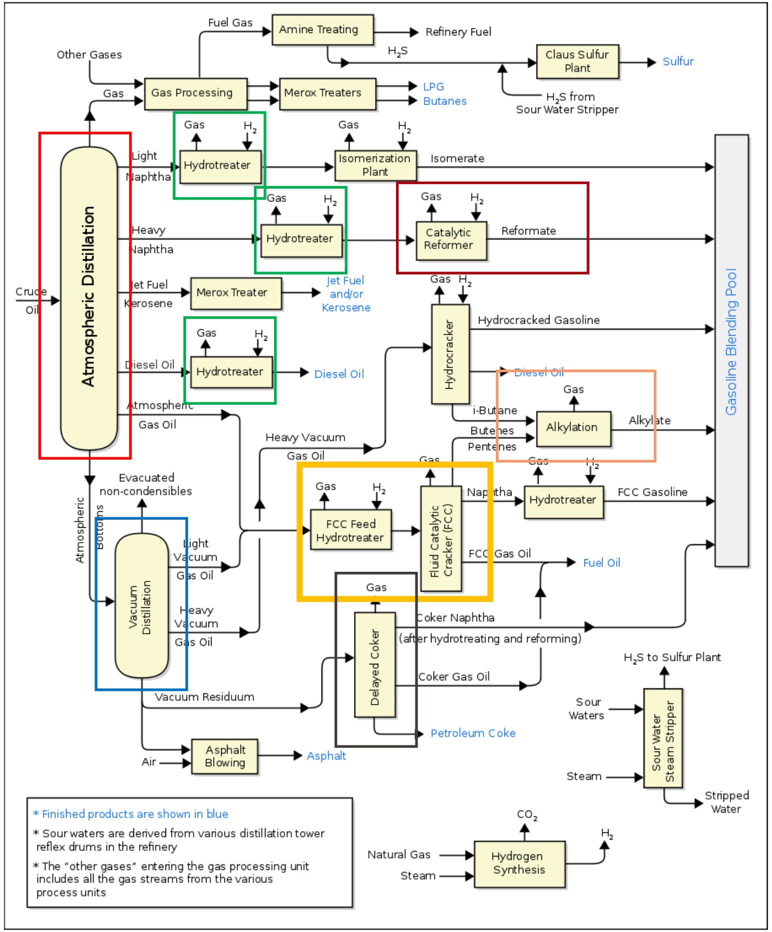
[a] Hat temperature is the temperature of the vapors rising to the gas oil drawoff tray in the fractionator.

[b] Carbon residue is that determined by Conradson residue test procedure (ASTM).

[c] For these items, the heater outlet temperature and the carbon residue, per se, do not have a significant independent effect.

- Heat and temperature favor light and heavy products
- Process control (i.e. stripping medium temperature) improves mid-weight products

(Syn)crude value chain



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Why catalytic cracking?

Paraffin → paraffin + olefin
Alkyl naphthene → naphthene + olefin
Alkyl aromatic → aromatic + olefin

Table 6.1 Thermal Versus Catalytic Cracking Yields on Similar Topped Crude Feed

	Thermal cracking		Catalytic cracking	
	wt%	vol%	wt%	vol%
Fresh feed	100.0	100.0	100.0	100.0
Gas	6.6		4.5	
Propane	2.1	3.7	1.3	2.2
Propylene	1.0	1.8	2.0	3.4
Isobutane	.8	1.3	2.6	4.0
n-Butane	1.9	2.9	0.9	1.4
Butylene	1.8	2.6	2.6	3.8
C_5+ gasoline	26.9	32.1	40.2	46.7
Light cycle oil	1.9	1.9	33.2	32.0
Decant oil			7.7	8.7
Residual oil	57.0	50.2		
Coke	0		5.0	
Total	100.0	96.5	100.0	102.2

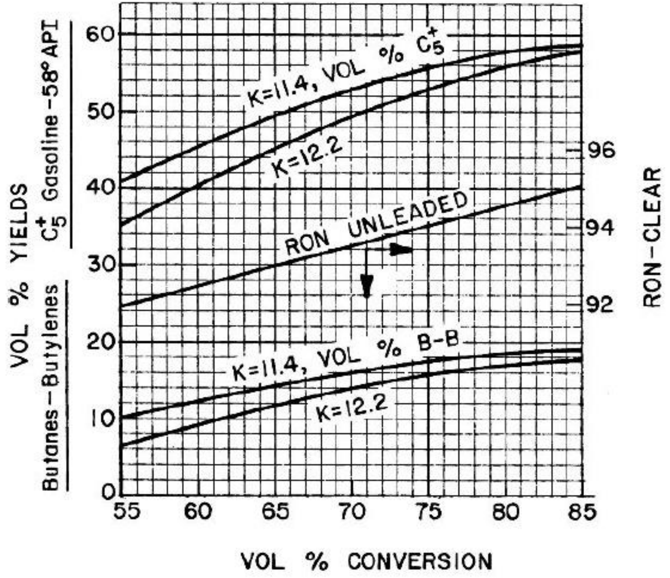
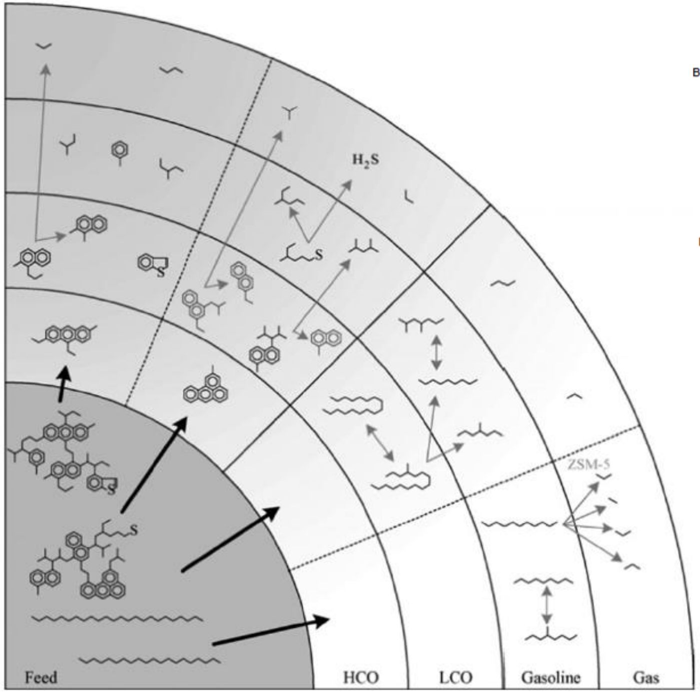
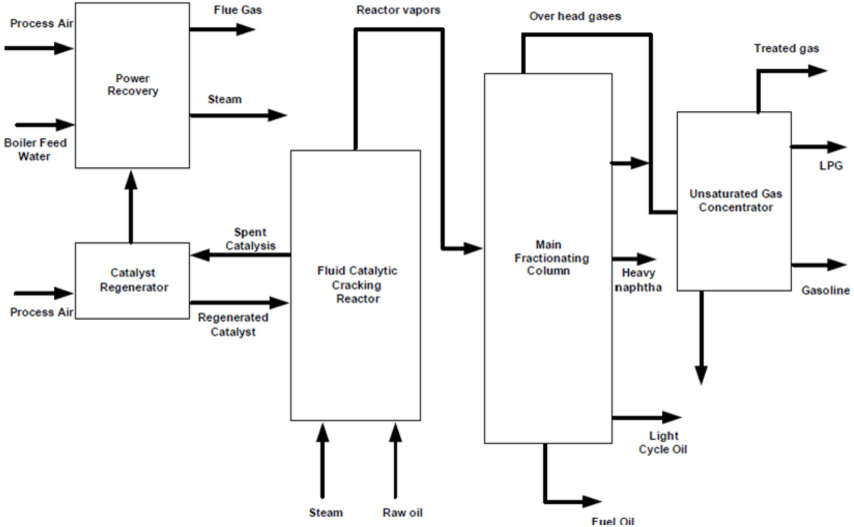


Figure 6.11 Catalytic cracking yields. Silica-alumina catalyst (butanes, butylenes, C_5^+ gasoline). The butane–butylene fraction typically contains about 40 vol% isobutane, 12 vol% n- butane, and 48 vol% butylenes.

Oil refinery – Catalytic processes

- Fluidized Catalytic Cracking (FCC)

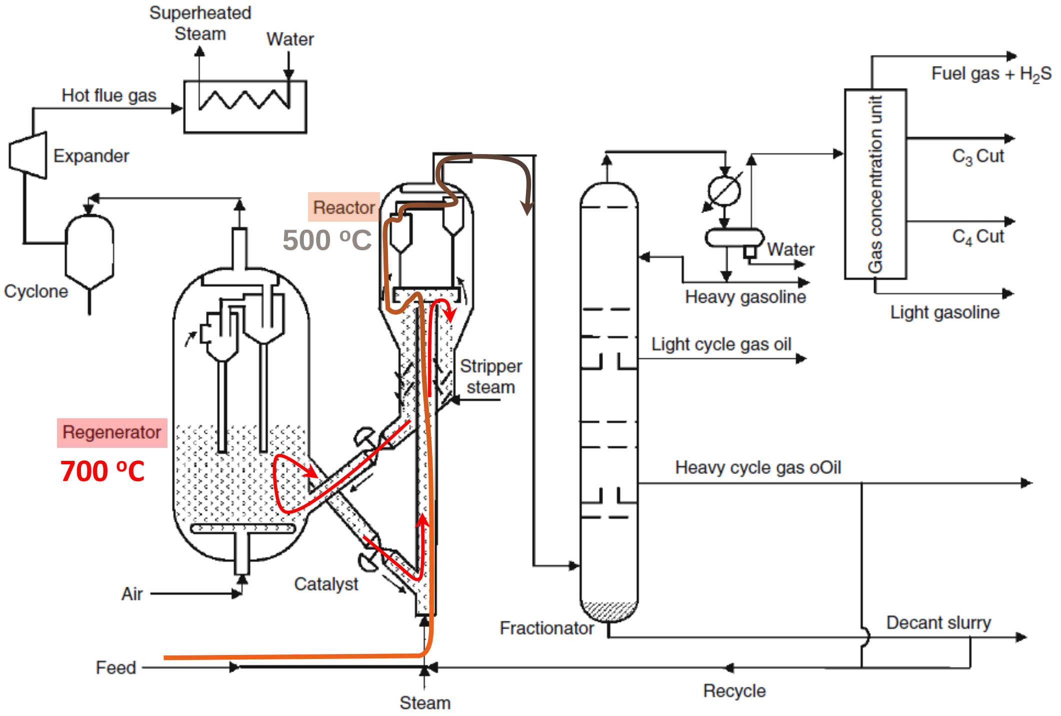




- Main process in oil refinery; heavy desulphurized feedstock → light, high octane gasoline.
- Feed: heavy gas oil (bp: 316 – 566 °C) = mix of aromatics, paraffins, and cycloparaffins.

Oil refinery – Catalytic processes

Fluidized Catalytic Cracking (FCC)



Valero Energy Corp
http://www.secinfo.com/dsvrp.uEe6.d.htm#1stPage

- Coke formation on catalyst (deactivation) requires regeneration of catalyst (coke burning).

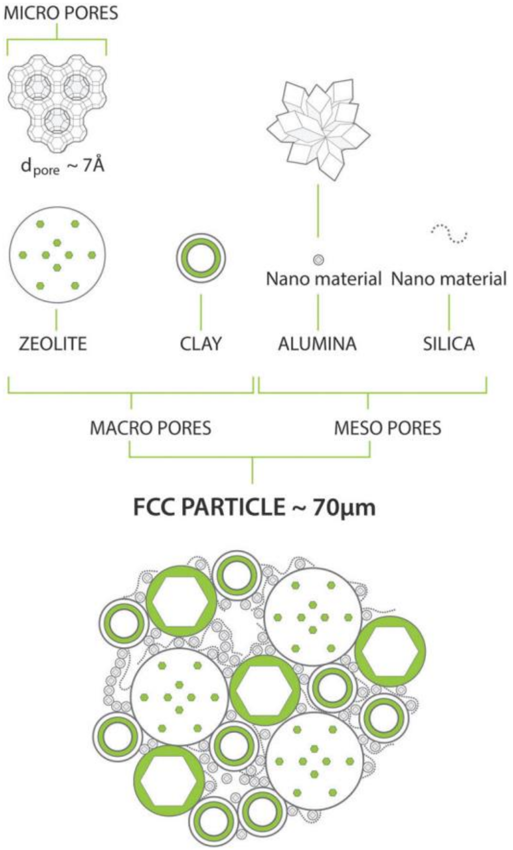
Oil refinery – Catalytic processes

- **Fluidized Catalytic Cracking (FCC)**

- Acidic catalysts promote the formation of saturated, branched, cyclic and aromatic hydrocarbons via the formation of a carbenium ion intermediate.

1) Historical catalysts: Amorphous Al-Si + 10-15 wt% Al_2O_3

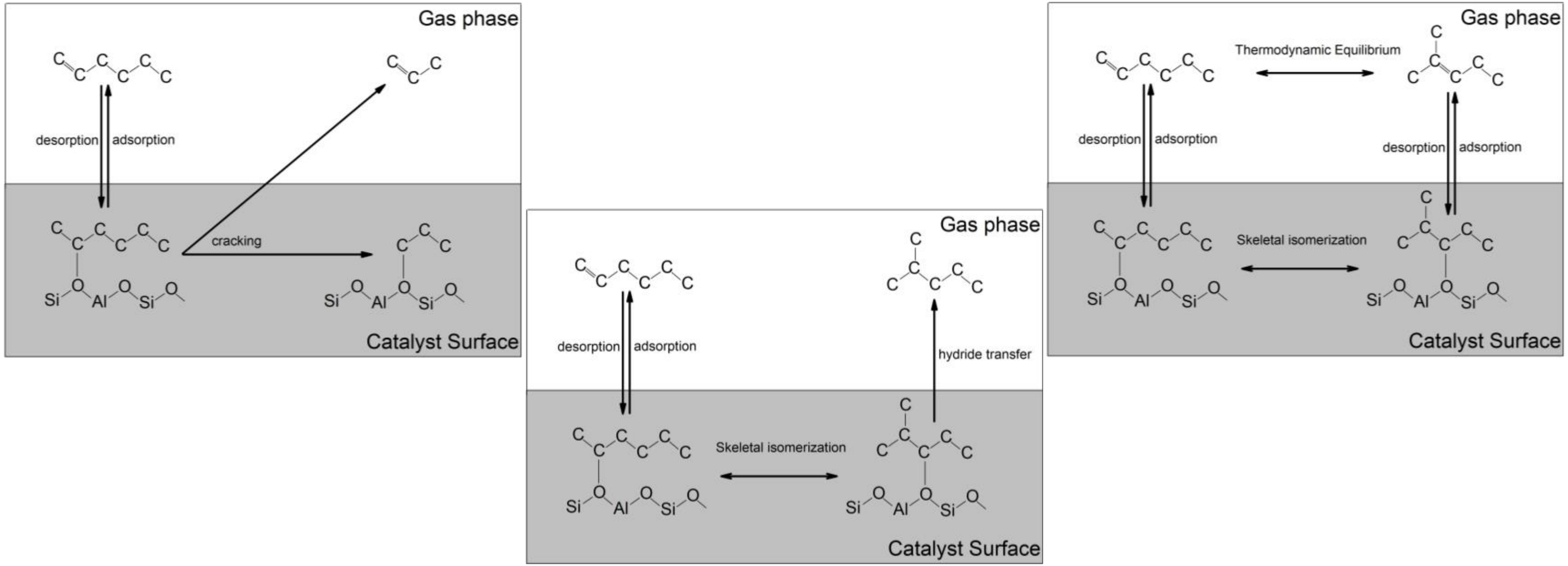
2.) Modern catalysts: 5-40 wt% crystalline Al-Si (zeolites) + Amorphous Al-Si



E. T. C. Vogt and B. M. Weckhuysen, Chem. Soc. Rev., 2015, 44, 7342

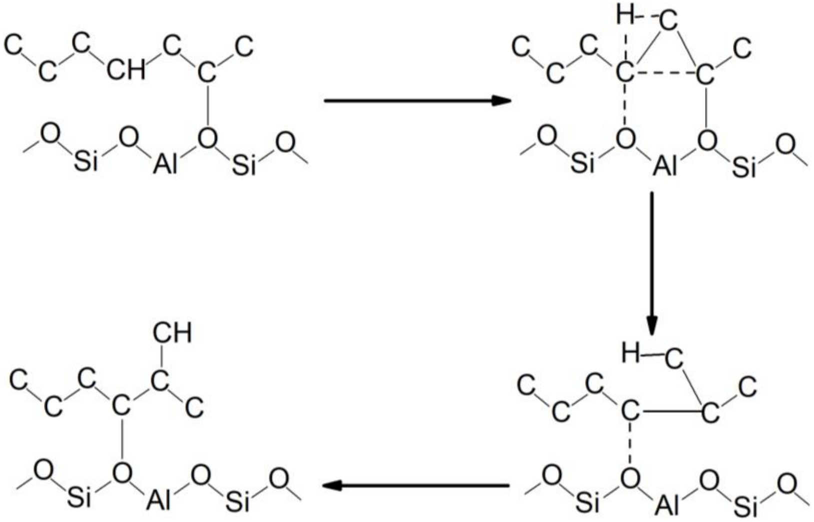
Oil refinery – Catalytic processes

- Fluidized Catalytic Cracking (FCC) – Mechanism of cracking reaction



Oil refinery – Catalytic processes

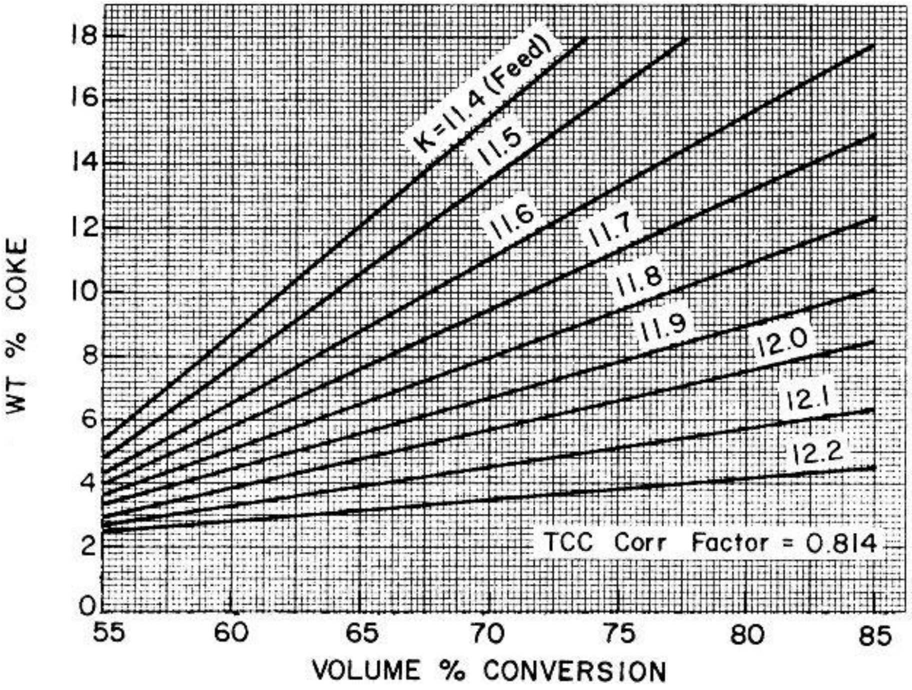
- **Fluidized Catalytic Cracking (FCC) – Mechanism of cracking reaction.**

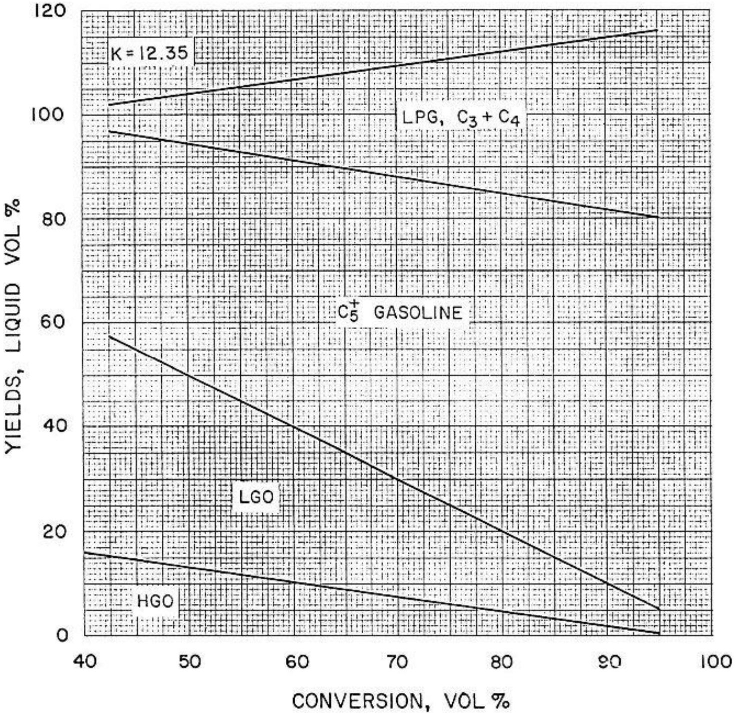


Skeletal isomerization

Conversion vs. yield profiles

Increasing conversion → more light products and more coke





Oil refinery – Catalytic processes

Hydrocracking

- Catalytic cracking with hydrogen. Allows also conversion of heavy distillates/residues into fuels.

Advantage: - Simultaneous removal of nitrogen (NH_3), sulphur (H_2S) and metals
- Less side reactions and less coke formation due to H-saturation of hydrocarbons

Disadvantage: - Expensive! Requires 300 – 500 m^3 H_2/t crude oil
- Harsh conditions: 270 – 450 °C, 80 – 200 bar

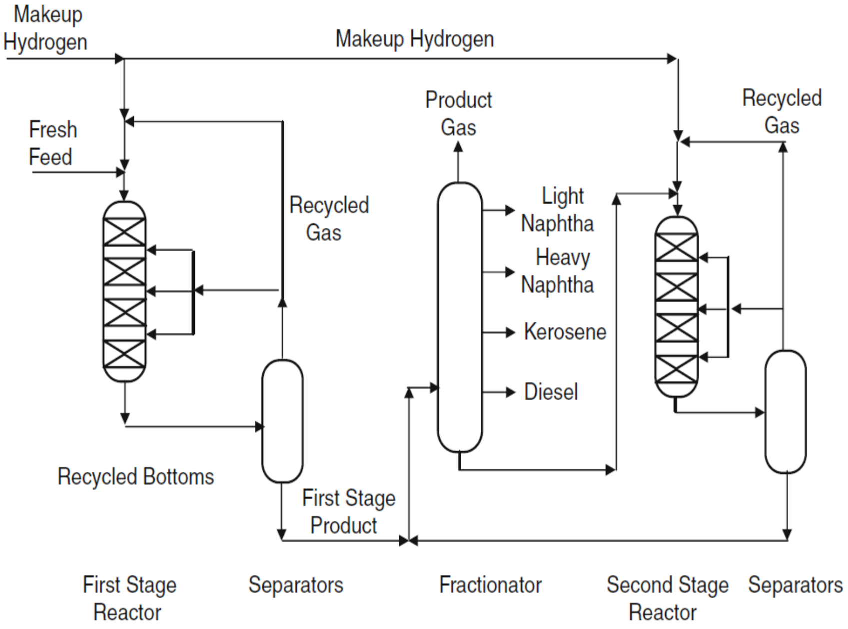
Hydrogenation Function	**Co/Mo**	**Ni/Mo**	**Ni/W**	**Pt or Pd**
	weak	medium	strong	Very strong

Cracking Function	**Al_2O_3**	**SiO_2-Al_2O_3**	**Zeolite**
	weak	strong	Very strong

Oil refinery – Catalytic processes

Hydrocracking

Typical two-stage hydrocracker



Hydrocracker Reactors

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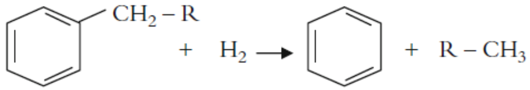
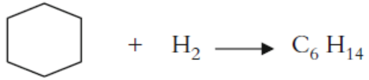
Alkane hydrocracking

$R-CH_2 \mid CH_2-R'$

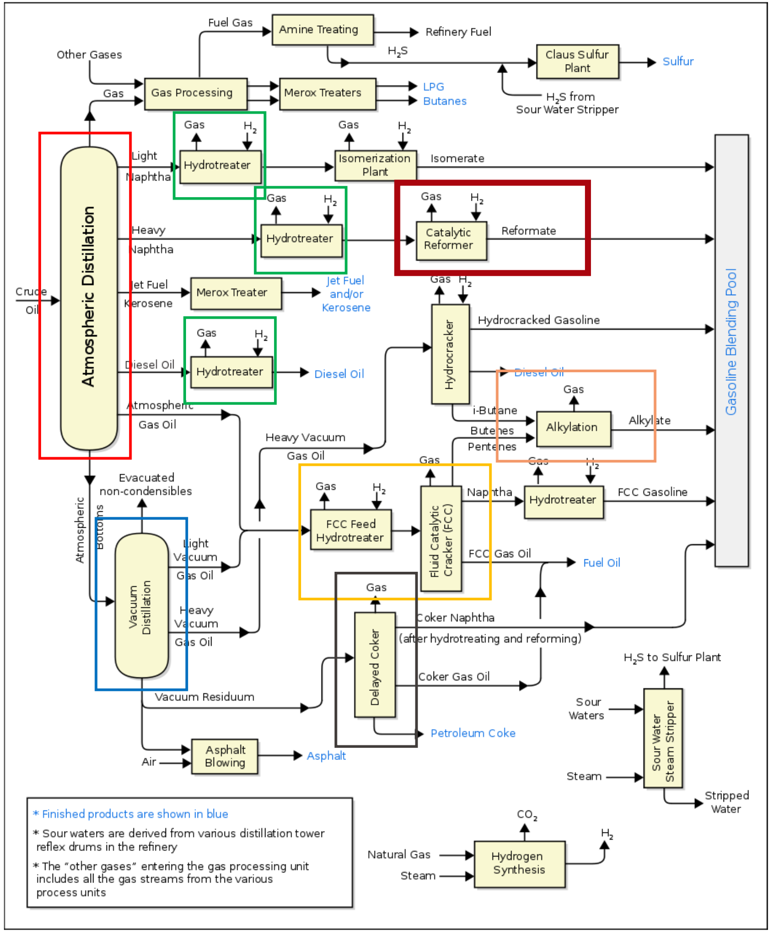
Hydroalkylation



Ring opening



(Syn)crude value chain



🟥 First distillation (topping)

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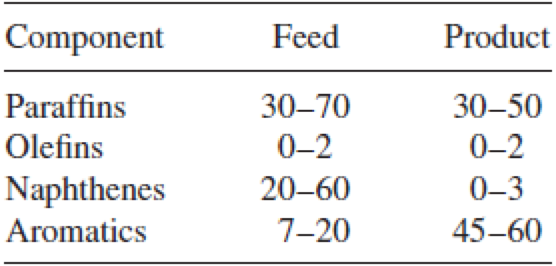
⬜ Coking

🟨 Fluid catalytic cracking

🟥 **Reforming**

🟧 Alkylation

What is reforming?



Component	Feed	Product
Paraffins	30–70	30–50
Olefins	0–2	0–2
Naphthenes	20–60	0–3
Aromatics	7–20	45–60

Paraffins (low RON) → Aromatics (high RON) + H_2

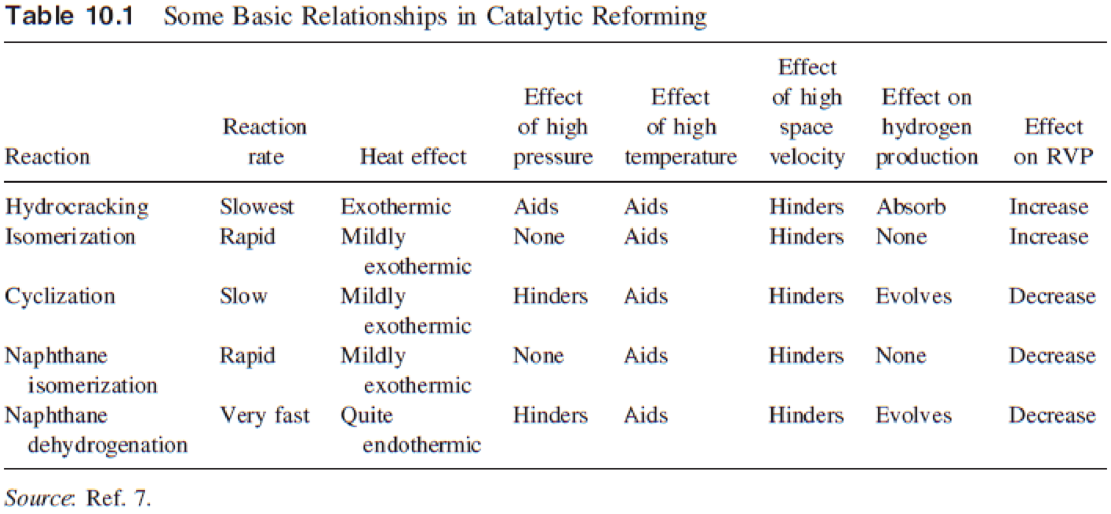


Table 10.1 Some Basic Relationships in Catalytic Reforming

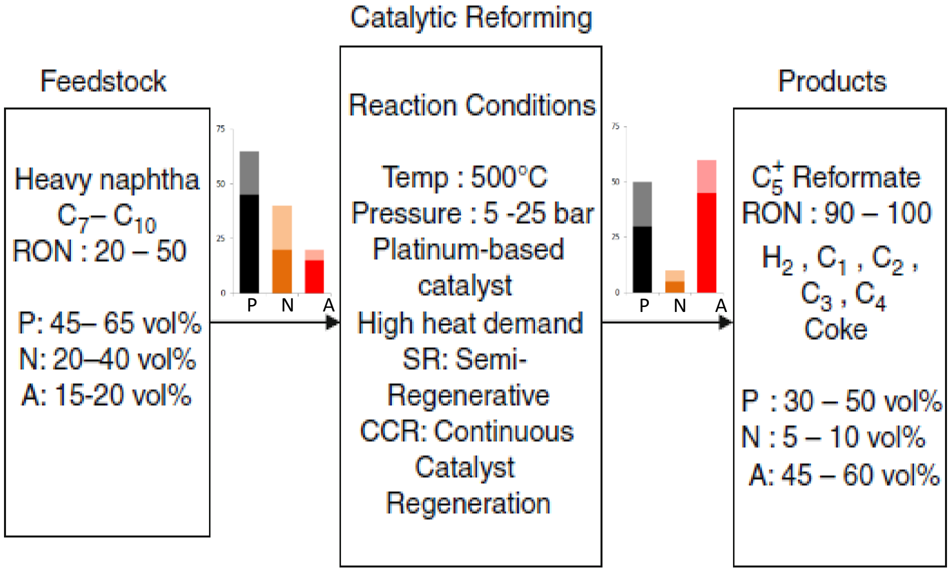
Reaction	Reaction rate	Heat effect	Effect of high pressure	Effect of high temperature	Effect of high space velocity	Effect on hydrogen production	Effect on RVP
Hydrocracking	Slowest	Exothermic	Aids	Aids	Hinders	Absorb	Increase
Isomerization	Rapid	Mildly exothermic	None	Aids	Hinders	None	Increase
Cyclization	Slow	Mildly exothermic	Hinders	Aids	Hinders	Evolves	Decrease
Naphthane isomerization	Rapid	Mildly exothermic	None	Aids	Hinders	None	Decrease
Naphthane dehydrogenation	Very fast	Quite endothermic	Hinders	Aids	Hinders	Evolves	Decrease

Source: Ref. 7.

Oil refinery – Catalytic processes

Catalytic Reforming

- Reforming = endothermic transformation of C_7-C_{10} hydrocarbons (low octane number, RON = 20-50) into aromatics and iso-paraffins (high octane number, RON = 90-100).



Catalytic Reforming

Feedstock

Heavy naphtha
C_7– C_{10}
RON : 20 – 50

P: 45– 65 vol%
N: 20–40 vol%
A: 15-20 vol%

Reaction Conditions

Temp : 500°C
Pressure : 5 -25 bar
Platinum-based catalyst
High heat demand
SR: Semi-Regenerative
CCR: Continuous Catalyst Regeneration

Products

C_5^+ Reformate
RON : 90 – 100
H_2 , C_1 , C_2 , C_3 , C_4
Coke

P : 30 – 50 vol%
N : 5 – 10 vol%
A: 45 – 60 vol%

P: paraffins, N: naphthenes (cycloalcanes), A: aromatics, RON = research octane number

Oil refinery – Catalytic processes

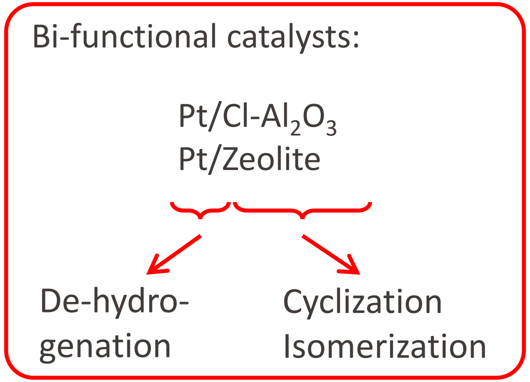
▪ Catalytic Reforming - Reactions

Desirable Reactions:

Dehydrogenation of naphthenes:

+ $3H_2$

Isomerization of paraffins:



Bi-functional catalysts:

$Pt/Cl\text{-}Al_2O_3$
Pt/Zeolite

De-hydro-genation

Cyclization
Isomerization

Dehydroisomerization of naphthenes:

+ $3H_2$

Dehydrocyclization of paraffins:

+ $4H_2$

Undesirable Reactions:

Hydrocracking and Hydrogenolysis:

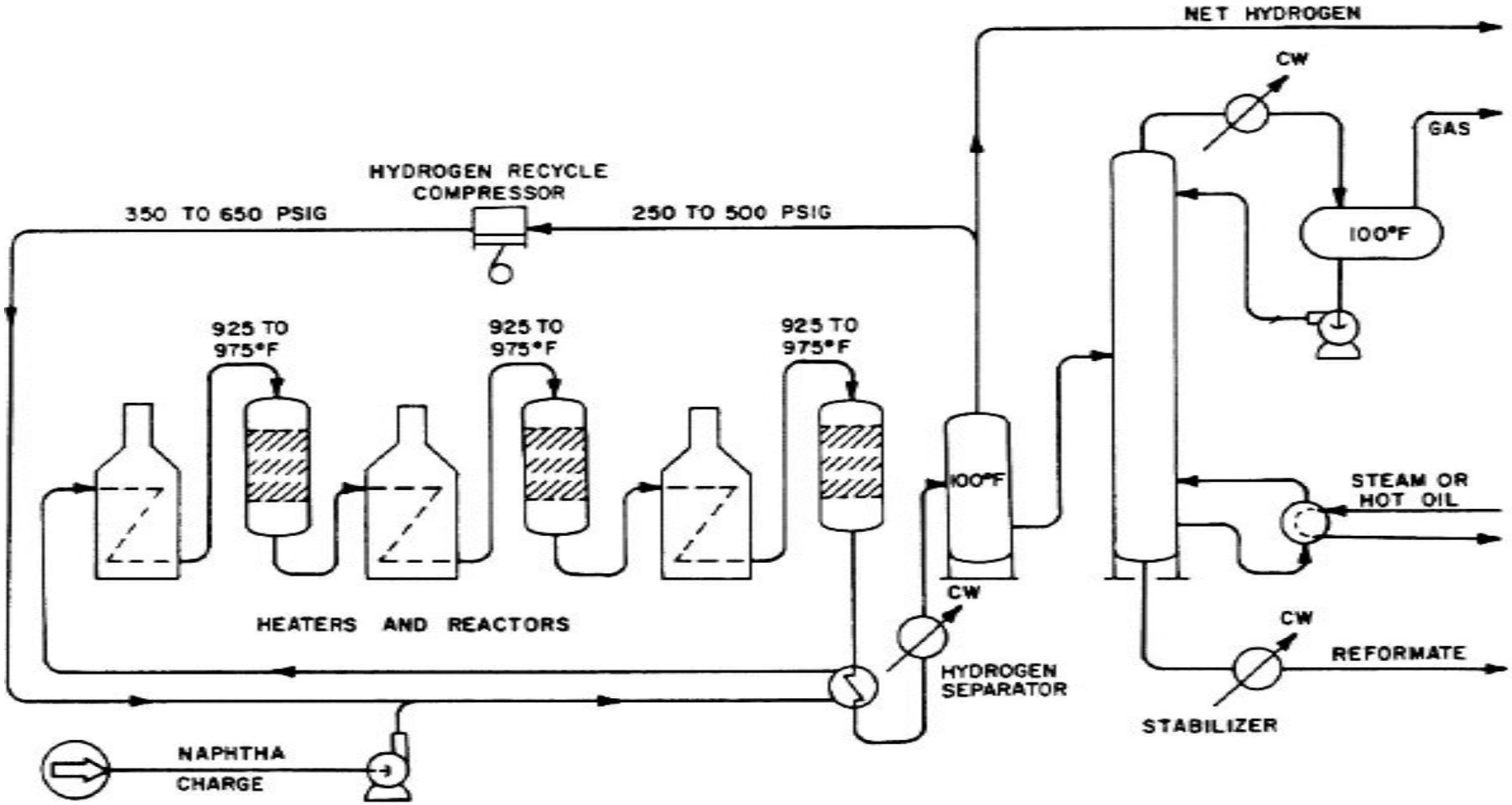
+ H_2

C_2 - C_6
(paraffins)

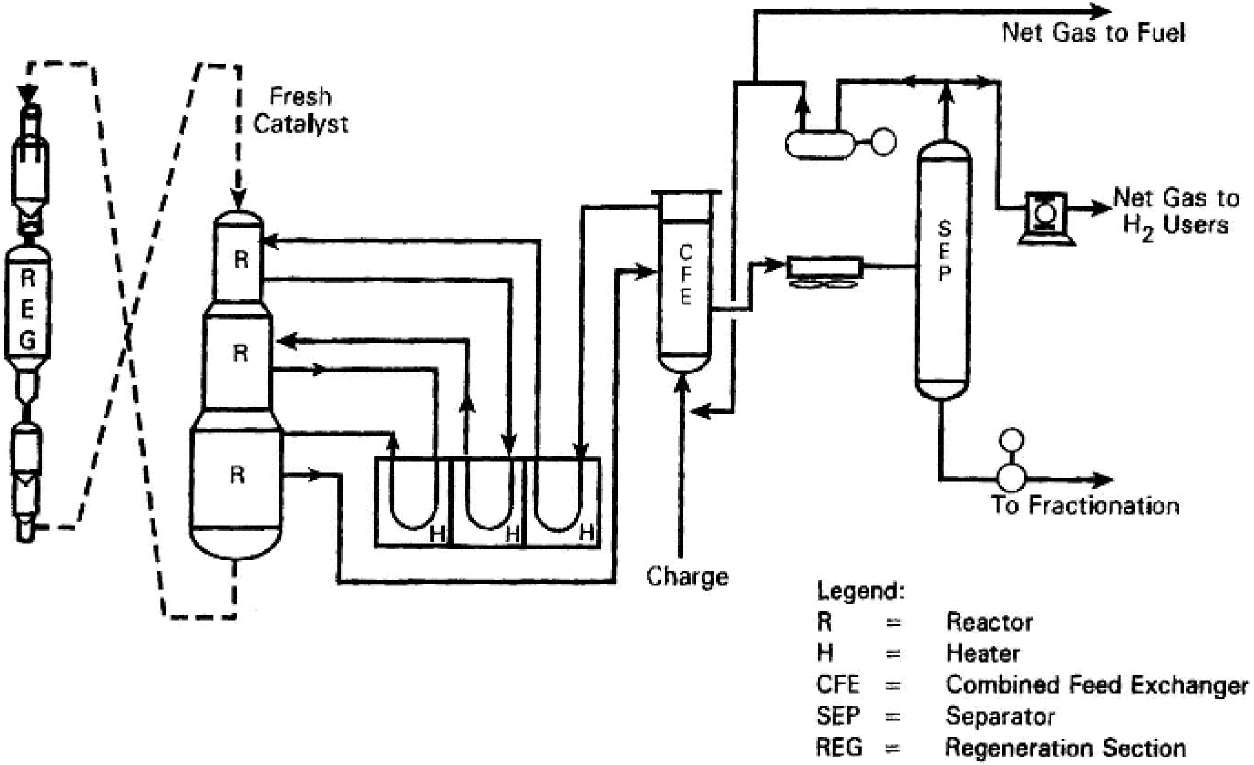
Coke formation:

C_8+ $9H_2$

Process configuration/ semiregenerative



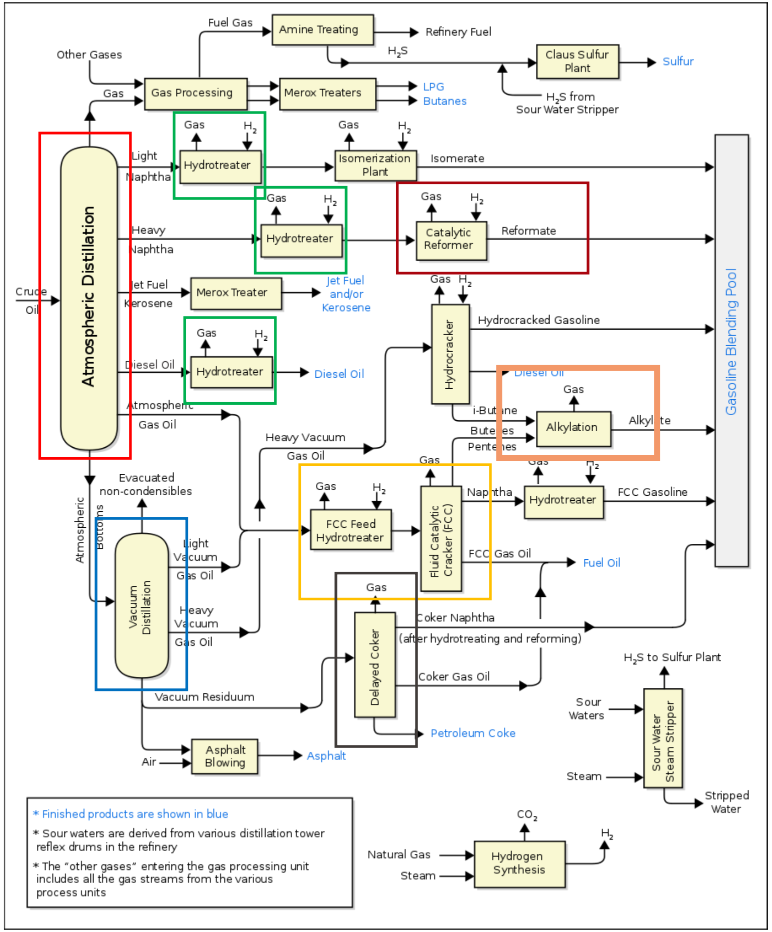
Process configuration/ continuous regeneration



Legend:

R	=	Reactor
H	=	Heater
CFE	=	Combined Feed Exchanger
SEP	=	Separator
REG	=	Regeneration Section

(Syn)crude value chain



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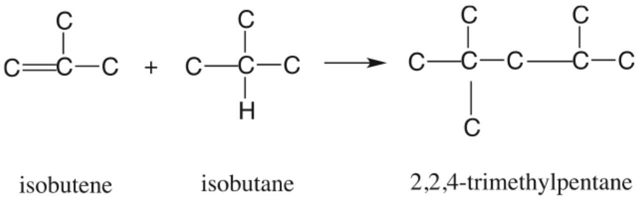
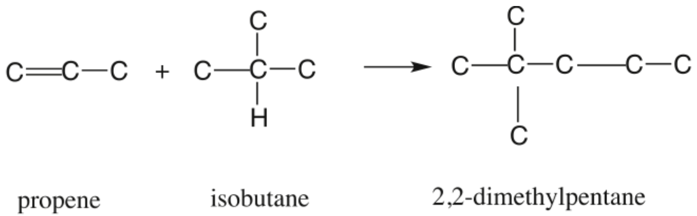
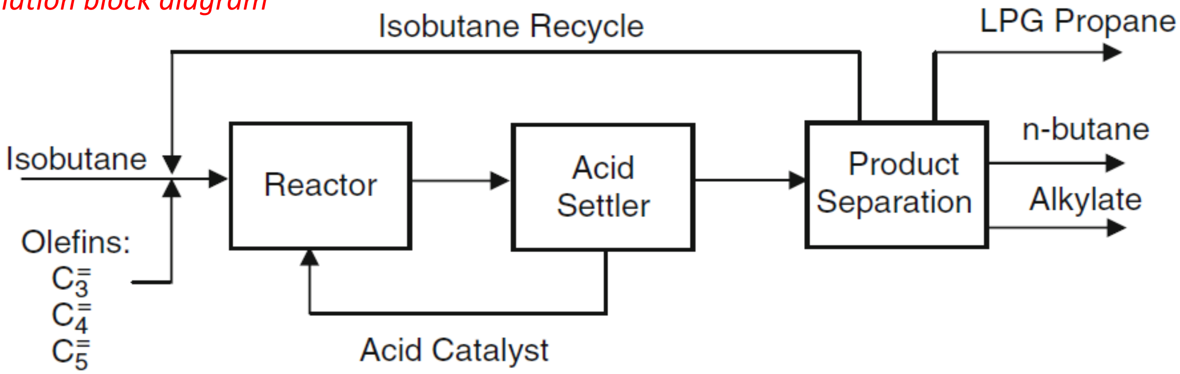
Alkylation

- Conversion of olefins(C_{3-5}) and iso-butane (iC_4) into higher branched gasoline with higher octane number (RON).





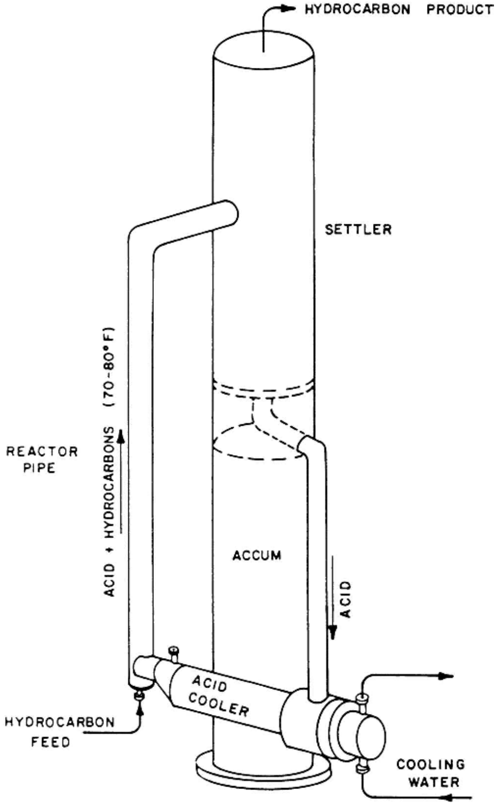
Alkylation block diagram



Historically:
→ thermal process
(500ºC, 200-400 bar)

Today:
→ catalytic process
(50ºC, 30 bar, strong acids: H_2SO_4 / HF)

Alkylation process



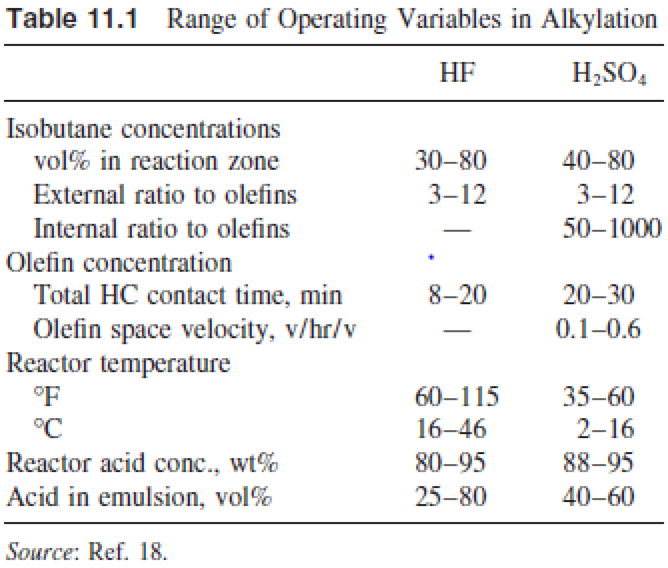


Table 11.1 Range of Operating Variables in Alkylation

	HF	H_2SO_4
Isobutane concentrations		
vol% in reaction zone	30–80	40–80
External ratio to olefins	3–12	3–12
Internal ratio to olefins	—	50–1000
Olefin concentration		
Total HC contact time, min	8–20	20–30
Olefin space velocity, v/hr/v	—	0.1–0.6
Reactor temperature		
°F	60–115	35–60
°C	16–46	2–16
Reactor acid conc., wt%	80–95	88–95
Acid in emulsion, vol%	25–80	40–60

Source: Ref. 18.