* Scrubbing operation:

S- contains acidic impurities.

→ scrubbing with monoethanol amine produces S (free of impurities)

→ H_2SO_4 manufacturing process:

Properties:

- Molecular weight : 98.08g/mol
- Melting point: ~~10.5°c~~ 10.5°c
- Boiling point: 348°c

Solubility: soluble in H_2O → produces large amount of heat

Production of H_2SO_4 by contact process

1. $S_{(s)} + O_2(g) \longrightarrow SO_2(g)$

2. $SO_2(g) + 1/2 O_2(g) \underset{\substack{V_2O_5 \text{ base} \\ \text{catalyst} \\ 450°c}}{\rightleftharpoons} SO_3(g)$

3. $SO_3 + H_2SO_4(l) \longrightarrow \underset{\text{(oleum)}}{H_2S_2O_7}$

4. $H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$ 97% yield of H_2SO_4
(Hydrolysis of $H_2S_2O_7$)

Catalyst		Promoter	Support
Pt/SiO_2	old catalytic system	k/Na/Ca	SiO_2
Pt/Al_2O_3			$SiO_2 \cdot Al_2O_3$
Pt/$SiO_2 \cdot Al_2O_3$			Al_2O_3
Pt/~~kiesdgahr~~ kieselguhr			kieselguhr ~~kiesdgahr~~ ↓ rock like substance with high silica content

V_2O_5/SiO_2
$V_2O_5/SiO_2 \cdot Al_2O_3$
V_2O_5/Al_2O_3
$V_2O_5/$ ~~kiesdgahr~~ kieselguhr

→ Drawbacks of platinum based catalyst:

1. High initial investment (0.5w% of Pt)
2. Poisoning effect (S-poisoning)
3. Rapid heat deactivation (for Pt based catalyst to be effective, Toptimum ~ 200-300°C but less than 500°C)
4. Fragile

→ Addvantage: Can handle pure feed (99.99% pure SO_2)

→ Advantages of V_2O_5 based catalyst:

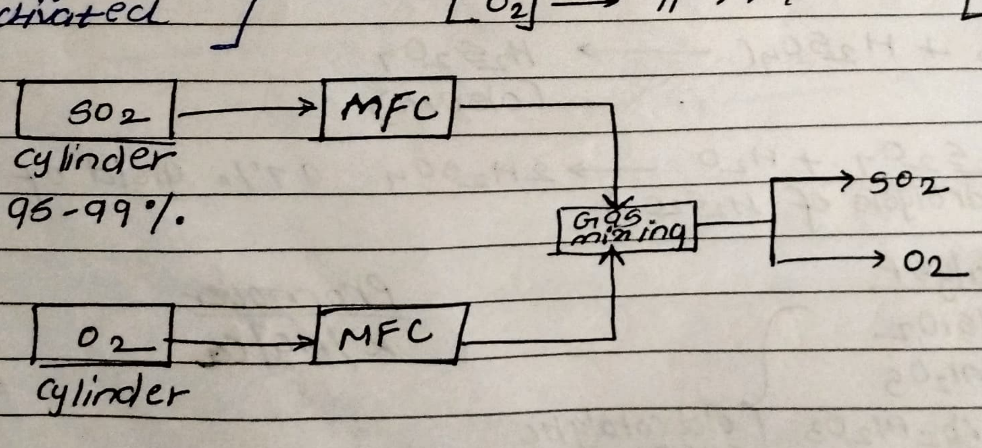
1. low initial investment 7-8% V_2O_5
2. Relatively immune to poisoning
3. Thermal stability (~800°C - 900°C)

→ Disadvantage: Feed should be diluted

(If we use conc^n feed catalyst will be deactivated)

$[SO_2] \to 7\text{-}10\%$
$[O_2] \to 11\text{-}14\%$

$\frac{[O_2]}{[SO_2]} \uparrow$



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V_2O_5 based catalyst:

$NH_4VO_3 \longrightarrow$ Ammonium Vanadate

1g of support (SiO_2) $\longrightarrow$ basis

S-1 Solid + $H_2O \longrightarrow NH_4VO_3(aq)$

S-2 Add in a drop wise manner to SiO_2 support and mix thoroughly $\rightarrow$ paste [$NH_4VO_3 + SiO_2$]

S-3 Calcination in a muffle furnace at a Temp of 450°c/500°c/550°C, air atmosphere, 4hrs

S-4 Post calcination, the furnace would be cooled to room temperature.

S-5 We will take out the catalyst, ball milling will be done to make into fine powder.

S-6 Pellets will be prepared for oxidation.

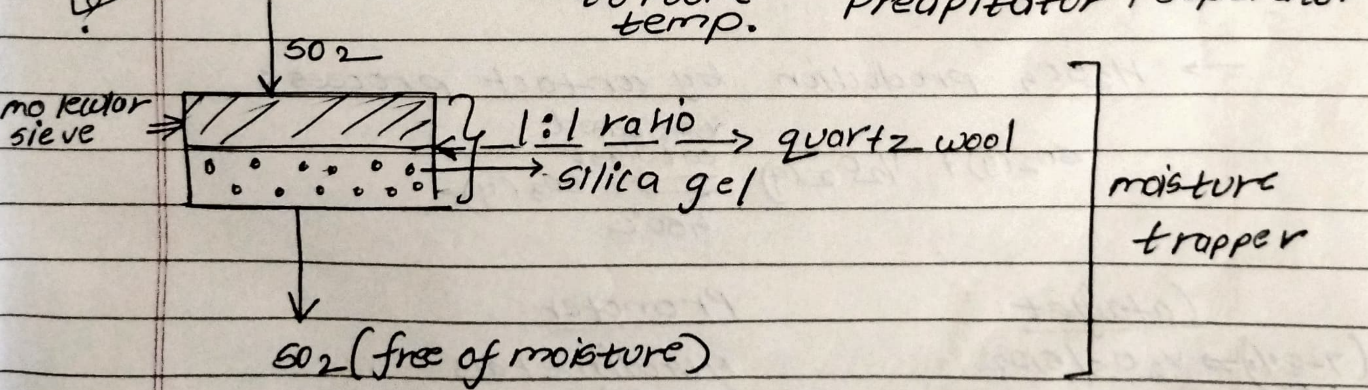
$$SO_2(g) + 1/2\,O_2(g) \rightleftharpoons SO_3(g)$$

Sources:

1. elemental $S + O_2 \longrightarrow SO_2$ [dust particles + moisture]

cooled to room temp. (for SO_2)

electrostatic ~~seperator~~ precipitator / cyclone seperator (for dust particles + moisture)



? 2. Pyrite source + O_2 ⟶ FeS_2 (40%–45% of S)
SO_2 → cooling needs to be done

↓

[Acidic ~~Active~~ impurities + dust + moisture] → F, Cl, Al based

↓

Scrubbing with amide soln

↓

SO_2

↓

moisture trapper (same as before)

↓

SO_2 (moisture free)

3. Smelter source
(non-ferrous sulfides)
PbS
CuS
ZnS ⇒ [zinch blend]
? MoS_2

→ H_2SO_4 production by contact process:

$$SO_2(g) + \frac{1}{2}O_2(g) \underset{450°C}{\overset{V_2O_5 \text{ based catalyst}}{\rightleftharpoons}} SO_3(g)$$

Catalyst:

(7–8% wt%) ⇒ V_2O_5/SiO_2
V_2O_5/Al_2O_3
$V_2O_5/SiO_2 \cdot Al_2O_3$
V_2O_5/kieselguhr

Promoter:

Alkalimetals
(Na/K) ⇒ 0.1 wt%

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Sources of SO_2:

1. elemental S
2. Pyrite (FeS_2) $\rightarrow$ 40-45% S $\xrightarrow{O_2}$ SO_2 $\rightarrow$ cooled
   $\uparrow$ (Dust particles, moisture)
3. Smelter [CuS, PbS, ZnS, MoS_2] non-ferrous sulfides $\xrightarrow{O_2}$ SO_2
4. $FeSO_4$ / spend H_2SO_4
5. H_2S sources [klaus process]

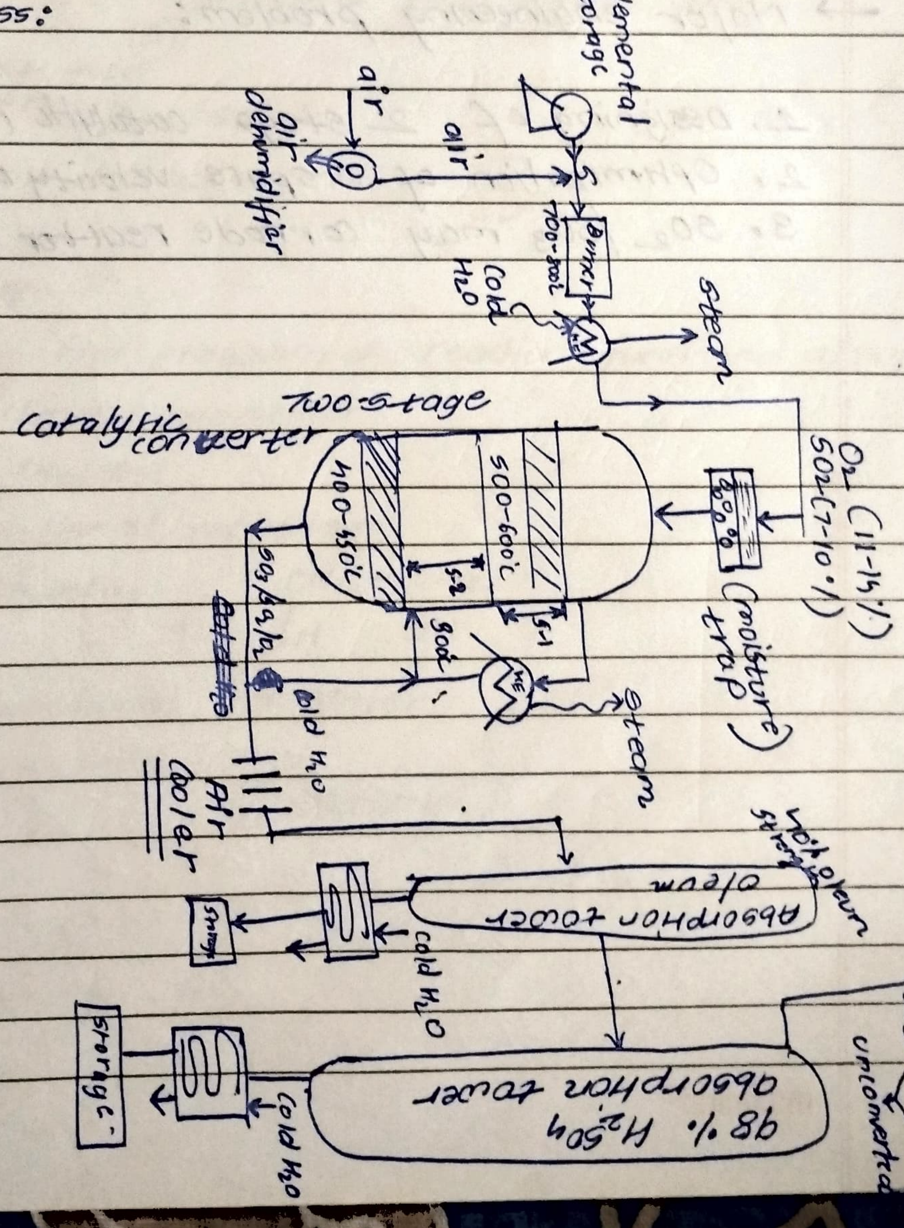
Δ 600-700°C
1. $H_2O + SO_2$
2. $Fe_2O_3 + SO_2$
   $\downarrow$
   sent to steel manufacturing industries.

SO_2 $\downarrow$ cooled down to RT

1. Dust particles
2. Moisture

remove

$\rightarrow$ Process:



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Reactor

Material of Construction ≡ steel
500-600°C

Stage 1: 80% of the Catalyst
yield = 80%

Stage 2: 70% of catalyst is utilized here.
(400-450°C)
yield = 97%

Catalyst: V_2O_5/SiO_2 pellets of roughly 3mm diameter

→ Major engineering problem:

1. Designing of 2 stage catalytic converter.
2. Optimization of space velocity of feed stream.
3. SO_2/SO_3 may corrode reactor wall.

$\tau = \frac{V}{\vartheta}$ sec

Polymer fundamentals: MW $\Rightarrow$ [$10^3 - 10^7$]

Monomer
$\downarrow$ monomer
Dimer
$\downarrow$ monomer
Trimer
$\downarrow$ monomer
Tetramer $\xrightarrow{\text{monomer}}$ pentamer $\rightarrow$ hexamer $\rightarrow$ ⋮

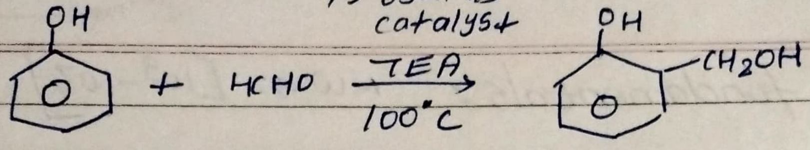
Monomer $\rightarrow$ = bonds (2 functionality)
or
$\rightarrow$ ≡ bonds (4 functionality)
or
$\rightarrow$ at least two Reactive fn'al groups:
[$-COOH$, $-OH$, $-NH_2$, $-\overset{O}{\overset{\|}{C}}-NH_2$, -- --]

Monomers:
(based on the presence of reaction functional groups)

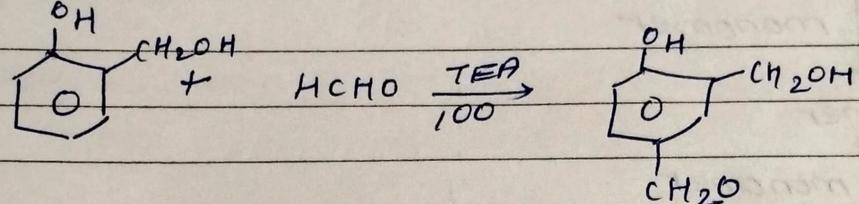
1. Unifunctional monomer
   eg - CH_3COOH
2. Bi-functional monomer
   eg $CH_2=CH_2$; $CH_2(OH)-CH_2(OH)$
3. Tri-functional monomer
   $CH_2(OH)-CH(OH)-CH_2(OH)$ [Glycerol]

Triethyl amine which is used as catalyst

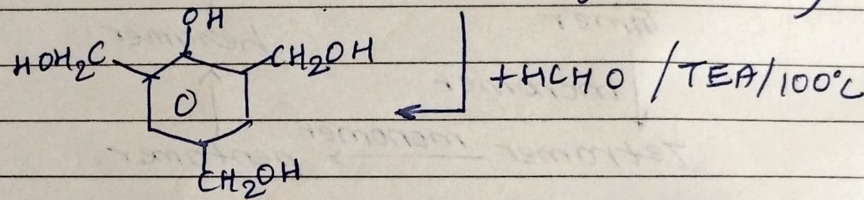
ex-1



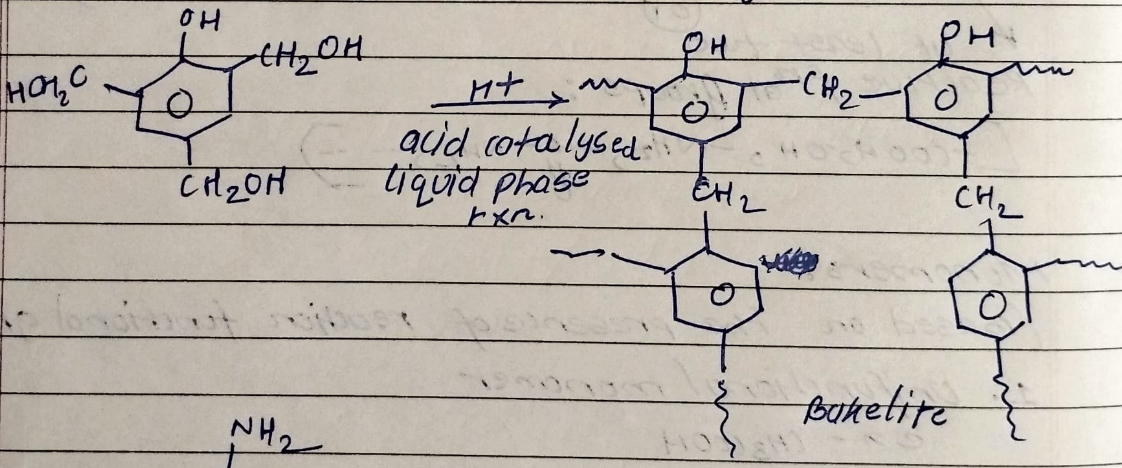
monomethylol phenol



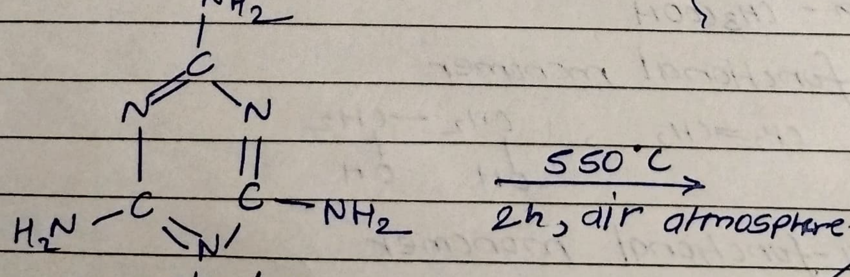
(Dimethylol phenol)



Trimethylol phenol
3 functionality



ex-2



Melamine
(monomer)

[White powdery material]

(yellow)
g-C_3N_4
graphitic carbon nitride
(metal free Polymer).

Use :
1. water splitting reactn
2. photocatalyst

water spliting → $H_2O \rightarrow H^+ + OH^-$
$hOH \rightarrow 2H_2O + O_2$

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→ Polymer :

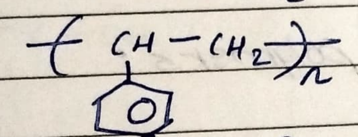
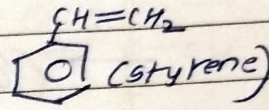
$n(CH_2=CH_2) \xrightarrow[70^\circ C,\ 6\ atm\ p]{Z\text{-}N\ catalyst} -[CH_2-CH_2]_n$

Poly thene.

Examples of polymer molecules :

1. Commodity polymer

a. $-(CH_2-CH_2-)_n$

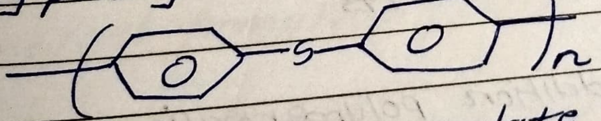
b.  Polystyrene  (styrene)

c. $-(CH-CH-)_n$ with Cl on the carbon — Polyvinyl chloride — vinyl chloride $CH_2=CH$–Cl

d. $-(CH_2-CH(CH_3)-)_n$ polypropelene

→ 2. Polymers in electronic application :

1. polyacetelene $-(CH=CH-)_n$
2. polyphenylene sulfide

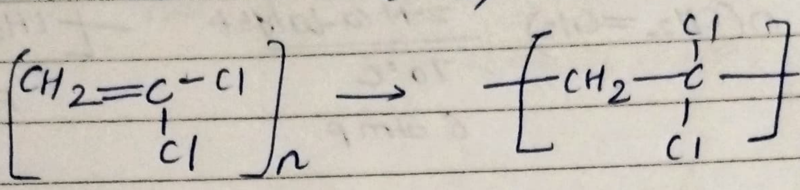


3. Polymethyle methacrylate $[CH_2=CH-COOH]$ → acrylic acid.

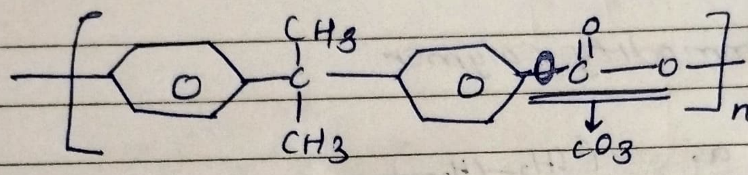
$[CH_2=C(CH_3)-COOCH_3]$

4. Silicone polymer $-[Si(CH_3)_2-O-]_n$

5. Vingledene dichloride (Poly)



6. Polycarbonate



→ Classification of polymers:

1. Based on molecular structure
2. Based on application of heat
3. Based on reaction mechanism

1. → Linear chain polymer molecules
   → Branched chain polymer
   → Network/ gel polymer

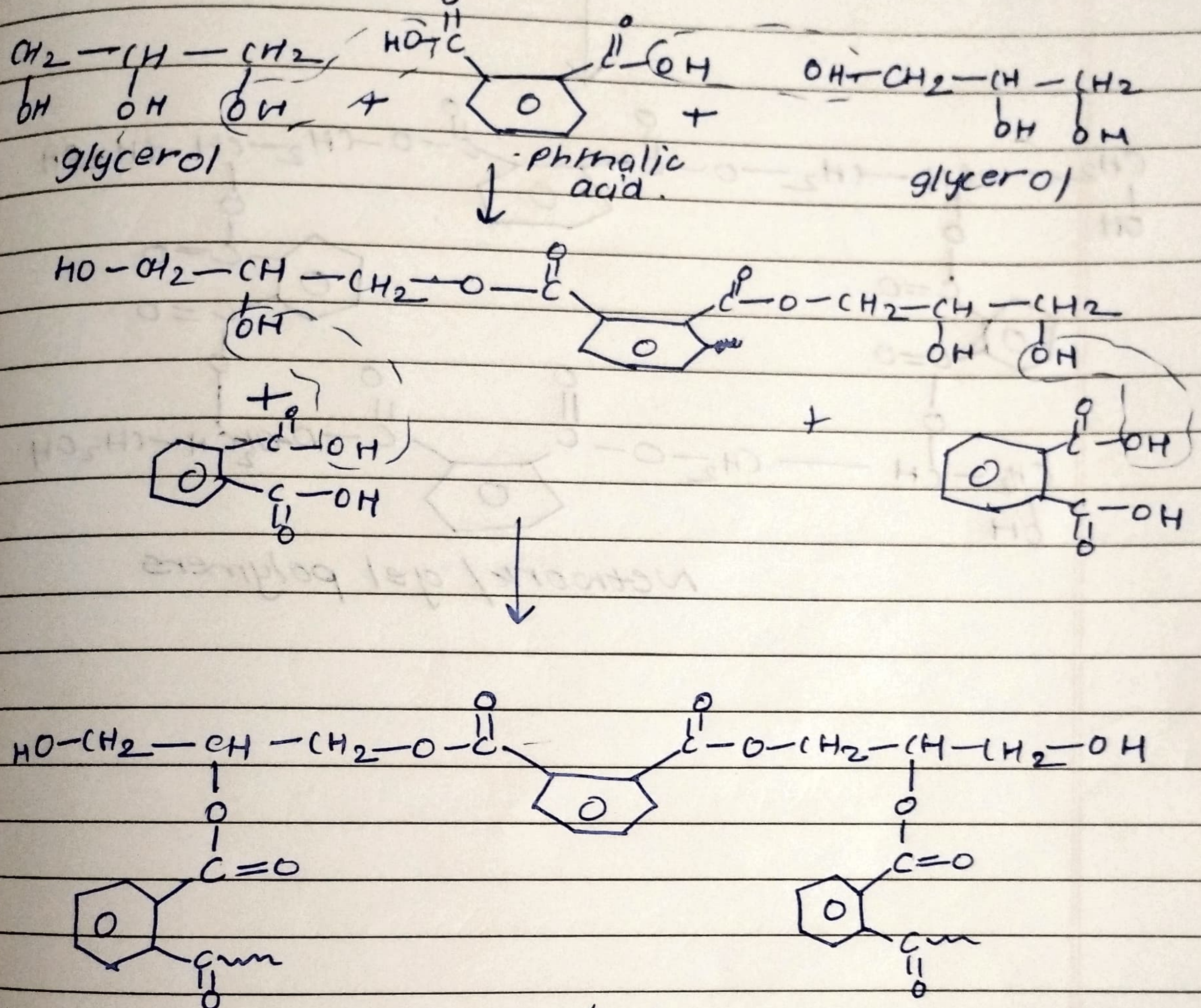
2. → Thermoplasts
   → Thermosetts

3. → Addition polymerisation
   → Condensation polymerisation

• Linear chain polymer molecules

$$n(CH_2=CH_2) \xrightarrow[70°C\ (6\ atm)]{ZN\ catalyst} -(CH_2-CH_2)_n$$

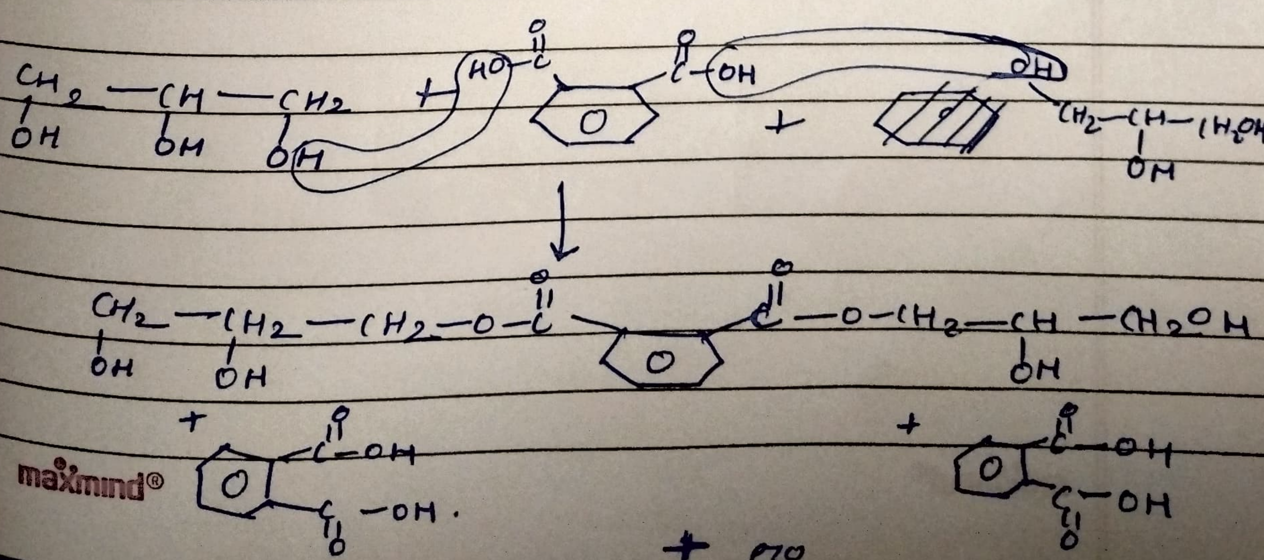
- Branched chain polymer



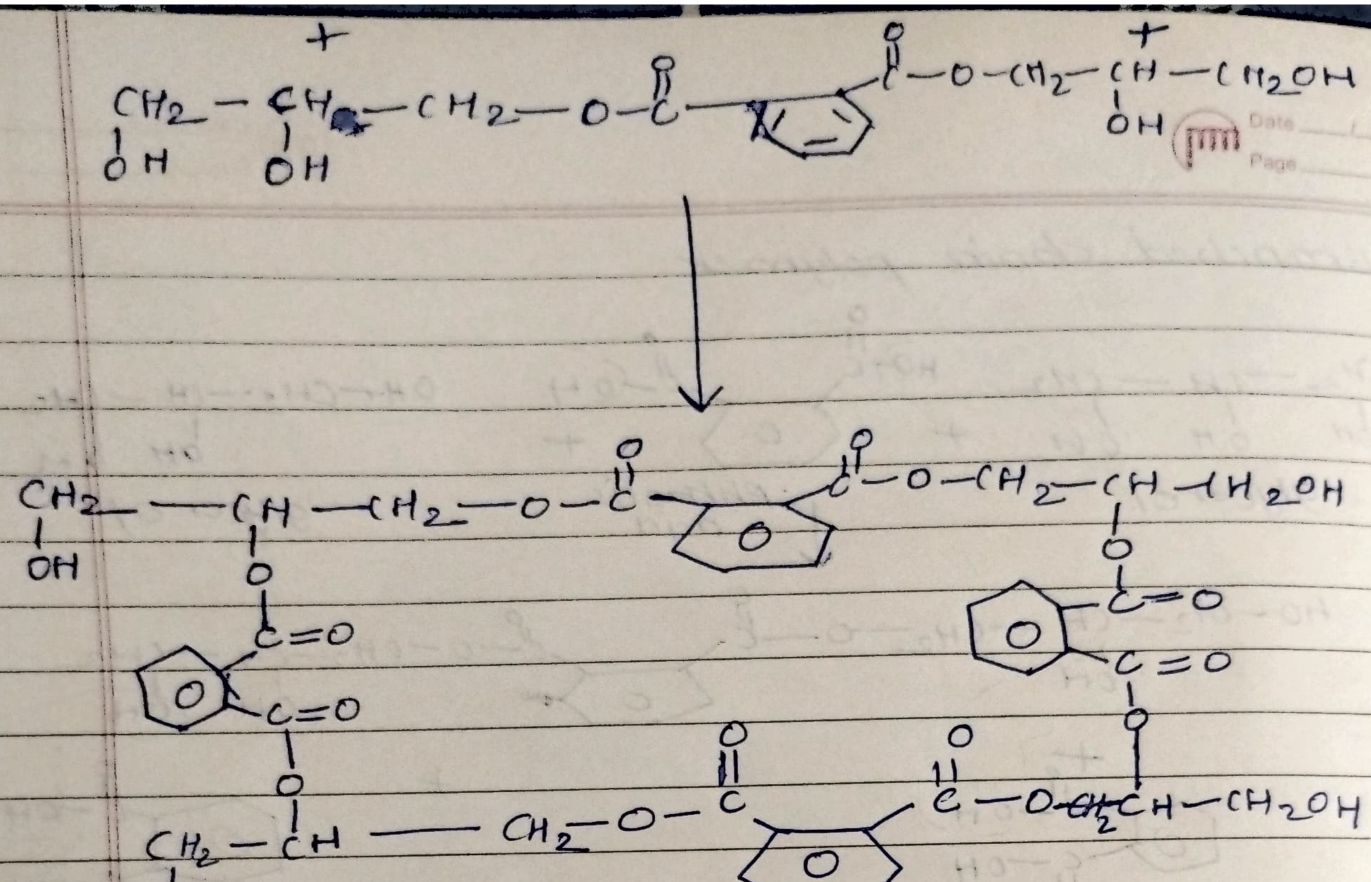
Branched chain polymer

- Network/gel formation (longer period of time required)

✓ property: Insoluble in any solvent.



+ PTO



Network/ gel polymers

→ Classification of polymer:

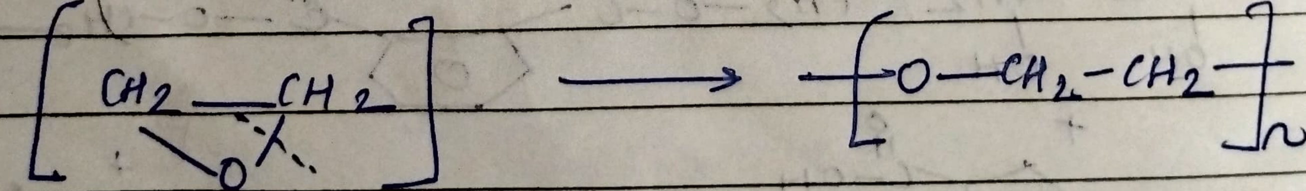
a) Based on molecular structure → linear
→ Branched
→ network/gel

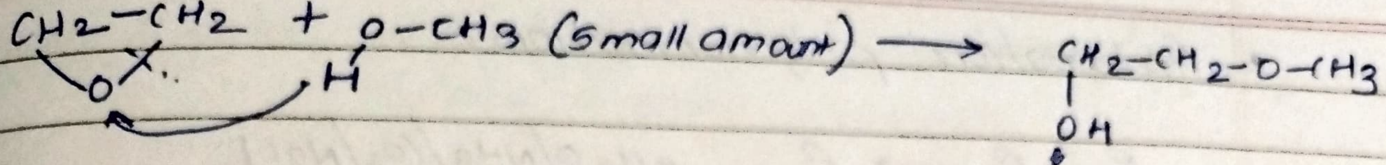
b) Based on reaction mechanism → addition polymerisation
→ Condensation polymerisation.

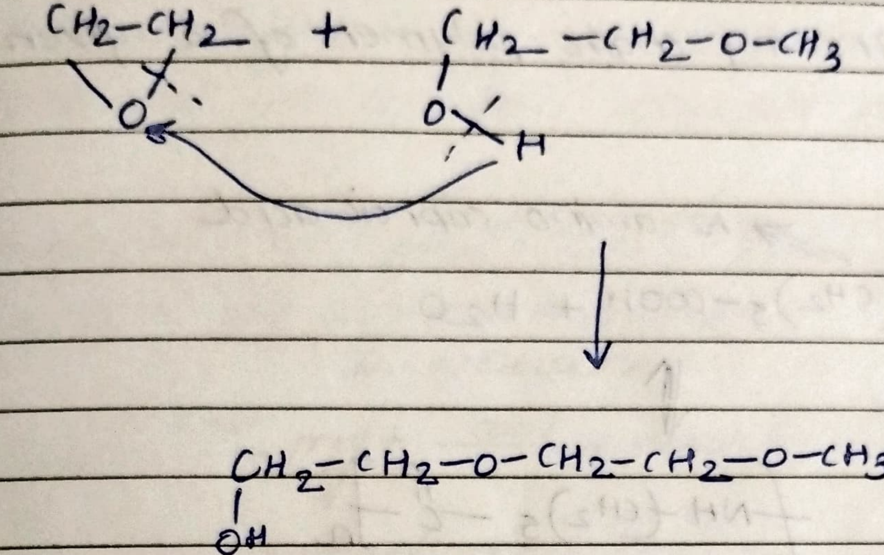
c) Based on application of heat → Thermosets
→ Thermoplasts

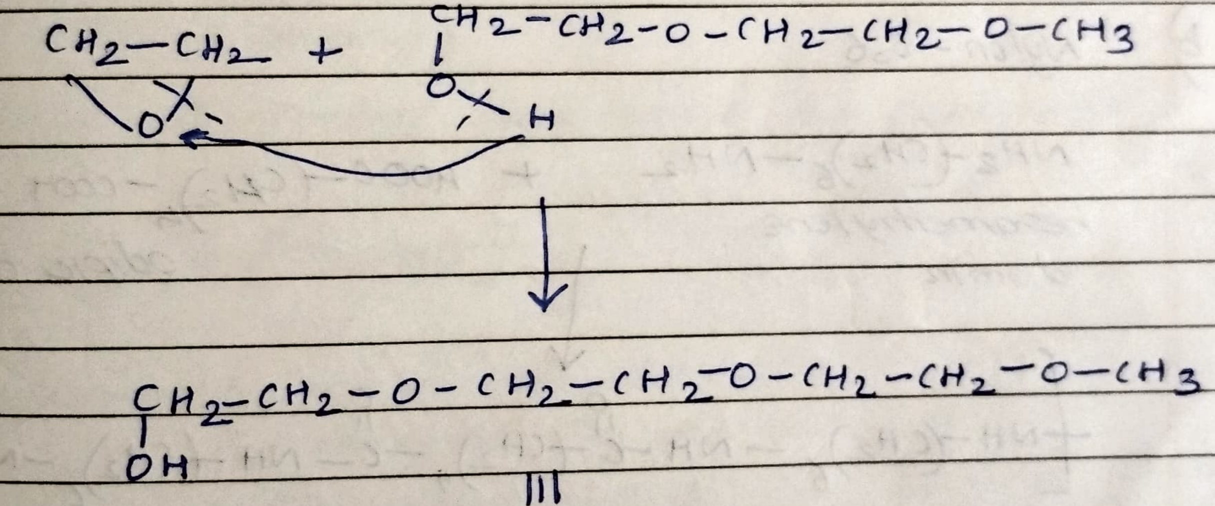
- Addition polymerisation:

1. $n[CH_2=CH_2] \xrightarrow[\substack{\text{7atm pressure} \\ \text{Ziegler-Natta} \\ \text{catalyst}}]{60-70^\circ C} -\!\!\left[CH_2-CH_2\right]\!\!-_n$

2. 

3. a) 

b) 

c) 

$$\underset{\displaystyle OH}{CH_2}-CH_2-\left[O-CH_2-CH_2\right]_n-O-CH_3$$

Applications:

a. Resin manufacturing

b. Manufacturing of fibrous material.

- Condensation polymerisation:

$$P_m + P_n \longrightarrow P_{m+n} + H_2O / NH_3 / CO_2 / NaCl$$

$m \neq n$

$P_m, P_n \Rightarrow$ growing chain polymer of a given monomer

a) Nylon-6

$NH_2 - (CH_2)_5 - COOH + H_2O$ → ω-amino caproic acid

$\rightleftharpoons$

$\left[NH - (CH_2)_5 - \overset{O}{\overset{\|}{C}} - \right]_n$

b) Nylon-6,6

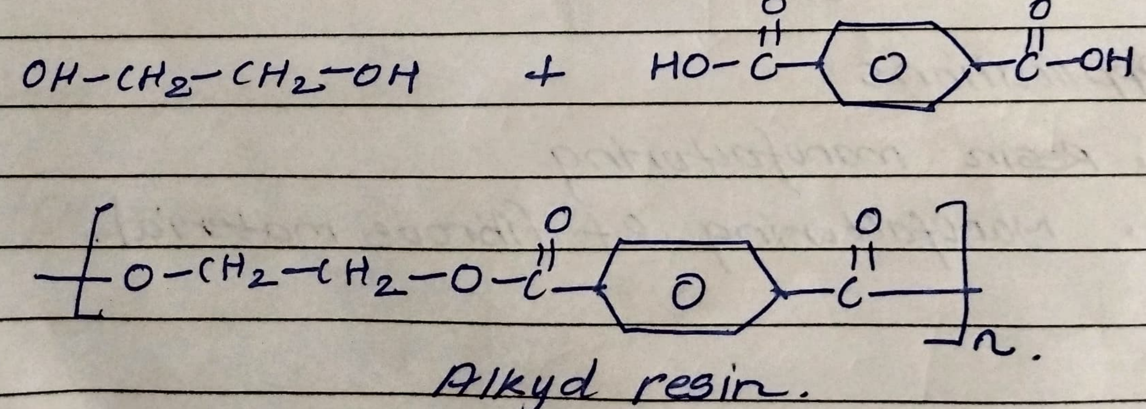
$NH_2 - (CH_2)_6 - NH_2$ + $HOOC - (CH_2)_4 - COOH$ + $NH_2 - (CH_2)_6 - NH$

hexamethylene diamin — adipic acid

$\downarrow$

$\left[NH - (CH_2)_6 - NH - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} - NH - (CH_2)_6 - NH - \right]_n$

c) Alkyd Resin



Alkyd resin.

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- Thermoplasts: Polymer should be linear chain / slightly branch chained molecules

Polymer $\xrightarrow{\text{heating}}$ Melts $\xrightarrow{\text{cool}}$ Solidify

[heating & cooling cycle can be performed several no. of times and it will not degrade the polymer].

- Thermosets: eg- Bakelite / melamine / urea-formaldehyde resin / phenol-formaldehyde resin.

polymers ⟶ 1. Branch chained
2. Network

polymer $\xrightarrow{\text{heat}}$ melt $\xrightarrow{\text{cool}}$ solidify $\xrightarrow{\text{heat}}$ degradation of polymer.

(curing of polymer takes place i.e. cross linking)

[heating & cooling cycle cannot be repeated]

→ Polyethylene $[CH_2-CH_2]_n$

Properties: 1. MW = 1500 - 1,00,000
2. Melting point = 85-110 °C
3. Density = a) 0.91 - 0.93 → Low density polyethylene (LDPE)
b) 0.96 → High density polyethylene (HDPE)
4. Consumption pattern: Powder, pellets, flakes

- Synthesis routes:

1. High pressure process (UK)
P = 1000-2500 atm
T = 100-300°C
Catalyst: Peroxide based catalyst.

2. Intermediate pressure process (USA)
P = 30-100 atm
T = 7100°C (Refer-150°C)
Catalyst: MoO_3/Al_2O_3 or Cr_2O_3/Al_2O_3

3. Low pressure process: (Italy + germany)
P = 7 atm
T = 60-70°C
Catalyst: Ziegler Natta

• Properties of polythylene by process (1):

1. LDPE (0.91–0.93)
2. Randomly distributed branches

• By process (2):

1. HDPE (0.96)
2. Highly crystaline
3. high tensile strength.

• By process (3):

1. HDPE

→ Polythylene production

We need ethylene

sources → Petroleum refinery

a. Catalytic cracking

b. Catalytic reforming

• Will not give pure $CH_2=CH_2$ ($CH_2=CH_2 + CH_4$)

• impurities will contain (S, O containing compounds).

↓

first seperate CH_4

↓

Purification

$CH_2=CH_2$ → $\boxed{\text{Pre-treater}}$ → (pure) $CH_2=CH_2$

↓

(RSH, thiophyne) (Phenol, etc.)

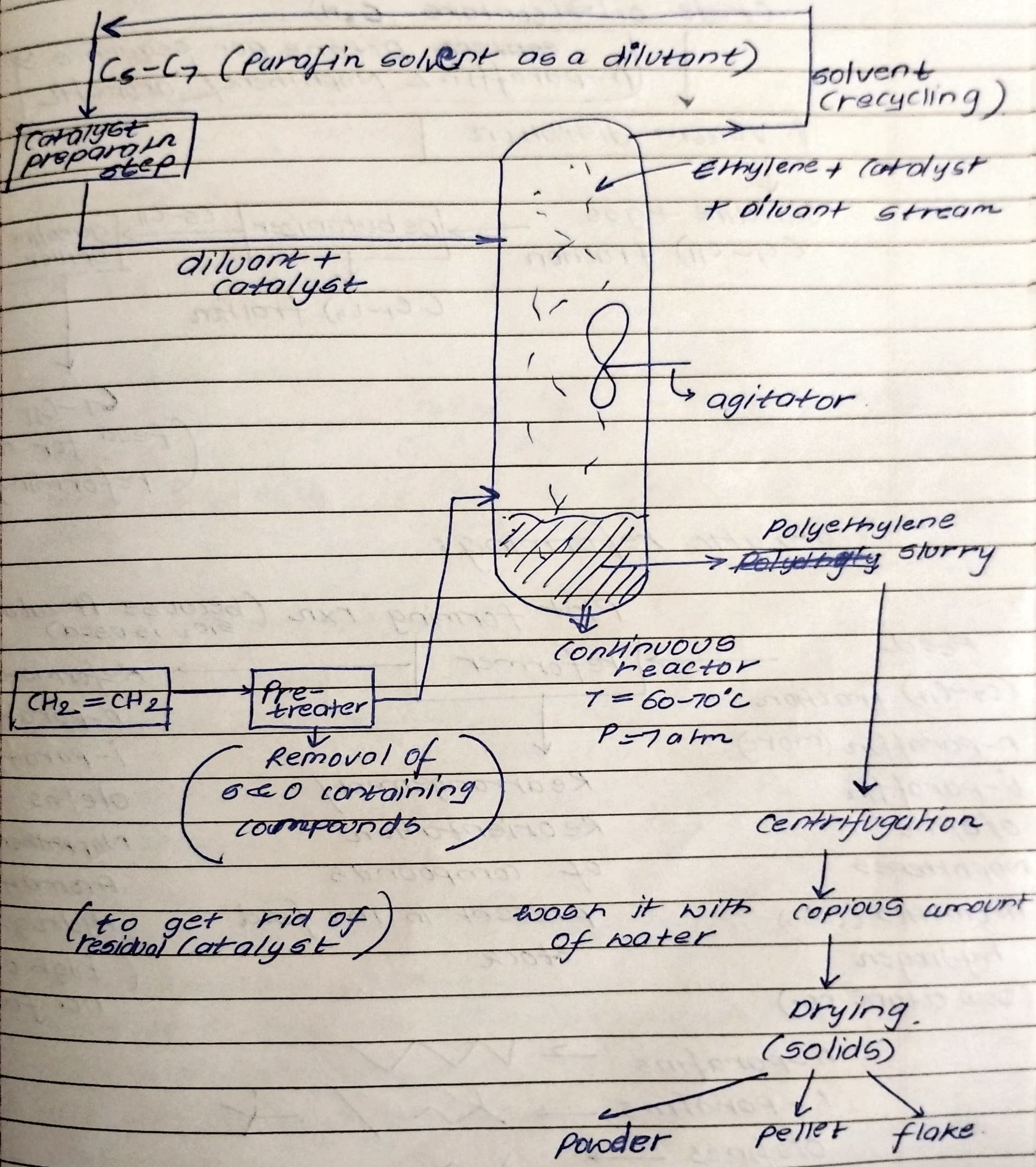
S, oxygen containing impurities

S, O

remove by dehydrosulfurisation

Deoxidation.

- Oxygen containing impurities cause deactivation of $TiCl_4/Al(C_2H_5)_3$ catalyst.



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→ **Petroleum refinery:**

Crude oil → (contains C, H)

~~[illegible]~~ Octane no. sequence
n-paraffin < Naphthene < aromatic

↓

| Vaccum distillation |

↓

Gasoline + gas ($C_1 - C_{11}$) fraction → | Debutanizer | → $C_5 - C_{11}$ → | gasoline spiller | → C_5-C_6

Debutanizer ↓ ($C_1 - C_4$) fraction

Gasoline spiller ↓ $C_7 - C_{11}$ (feed for catalytic reforming)

→ **Catalytic reforming:**

Plat forming rxn (because Pt catalyst on SiO_2 is used)

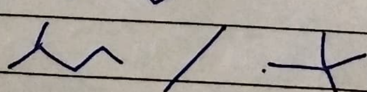
Feed ($C_7 - C_{11}$) fraction → | reformer | → Reformate

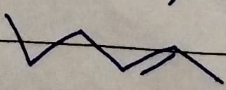
Feed:
n-paraffin (more)
i-paraffin
olefine
Naphthenes
Aromatics (less)
hydrogen
(low octane no.)

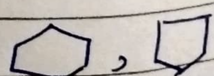
Reformer ↓ Rearrangement / Reorientation of compounds present in the feed stock

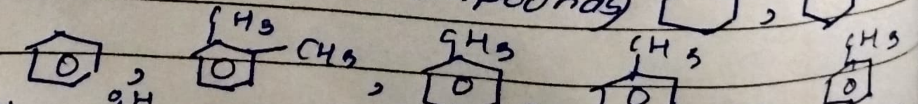
Reformate:
n-paraffin
i-paraffin
Olefins
Naphthenes
Aromatics
Hydrogen
(high octane no. fuel)

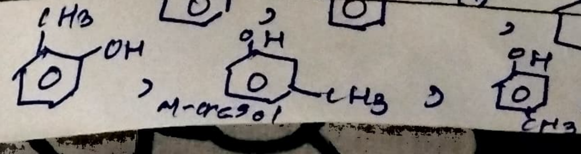
n-parafins → 

i-parafins → 

Olefines → 

Naphthenes → (cyclic compounds) 

Aromatics → 

o-cresol  p-cresol

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Catalyst and Rxn conditions:

$T = 450 - 500°C$

$P = 10 - 75$ atm

Catalyst = Pt/SiO_2

$Pt/SiO_2-Al_2O_3$

Regenerative catalyst:	Non-regenerative catalyst:
$Pt = 0.3 - 0.5$ wt%	$Pt < 0.3$ wt%

Other Catalysts:

MoO_3/SiO_2	Cr_2O_3/SiO_2	$MoO_3-Cr_2O_3/SiO_2$
MoO_3/Al_2O_3	Cr_2O_3/Al_2O_3	$MoO_3-Cr_2O_3/Al_2O_3$
$MoO_3/SiO_2-Al_2O_3$	$Cr_2O_3/SiO_2-Al_2O_3$	$MoO_3-Cr_2O_3/SiO_2-Al_2O_3$
10wt%	10wt%	10wt%
Mono-metal oxide catalyst		Bi-metal oxide catalyst

⇒ Reactions in a reformer unit.

1. Dehydrogenation
2. Isomerisation
3. Paraffin cracking.
4. Hydrogenation (only this rxn is exothermic)
5. Paraffin dehydrocyclisation
6. Naphthene isomerisation & dehydrogenation.
7. Hydrodesulfurisation
8. Denitrogenation
9. Deoxydation
10. Combination.

10% ↓ (1–6)

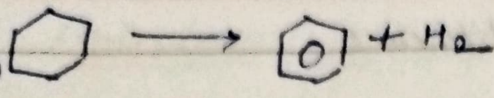
90% ↓ (7–10)

used for S, N, O containing compounds in feedstock

T, P & catalyst remains same for all 10 rxn.

Cyclohexane Benzene

1\.

a) 

2a b) $CH_3-CH_2-CH_3 \longrightarrow CH_3-CH=CH_2 + H_2$

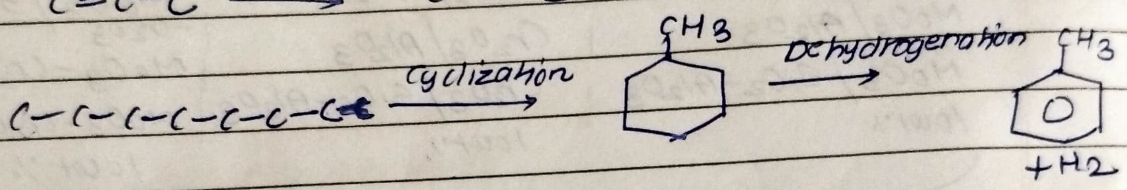
n-paraffin

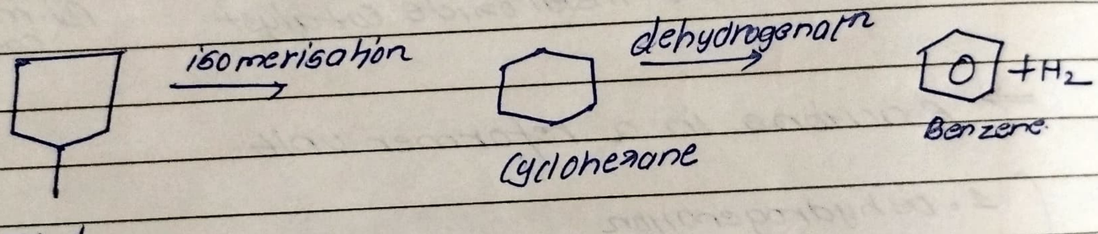
2\. $C-C-C-C-C \longrightarrow C-C-\underset{|}{\underset{C}{C}}-C + C-\overset{C}{\underset{C}{C}}-C$

3\. $C-C-C-C-C-C-C-C-C \longrightarrow C_4 + C_4 + H_2$

n-octane saturated unsaturated

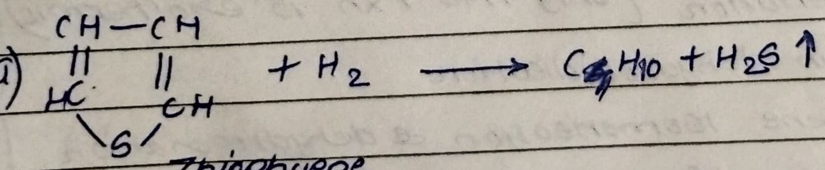
4\. $C=C-C \xrightarrow{+H_2} C-C-C$

5\. 

6\. 

methyl-cyclopentane. Cyclohexane Benzene

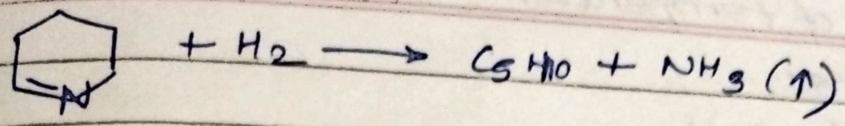
7\.

a) 

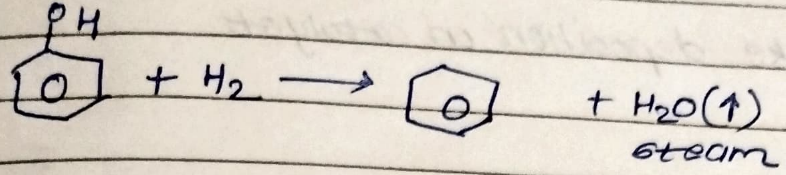
Thiophyene

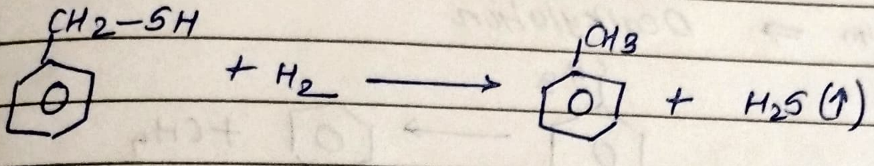
b) $R-SH + H_2 \longrightarrow RH + H_2S$.

Mercapta

8. 

N-cyclopentene

9. 

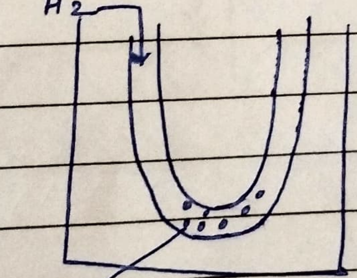
10. 

→ **Reformer:** Combination of furnace + fixed bed reactor.

* Catalytic reforming contd...

Catalyst characteristics:

1. Acidic surface sites → [will facilitate isomerisation and cyclization rxn]
2. Metallic bonds (interaction b/w metal & support)
   - → [facilitates hydrogenation rxn]
   - → H_2- chemisorption [Active metallic surface sites]



PID controlled furnace

Ramping:
RT → 950°C
@ 5°/min.

To incorporate acidic sites on catalyst surface we perform halogenation operations usually chlorination is done.

Effect of temperature & pressure:

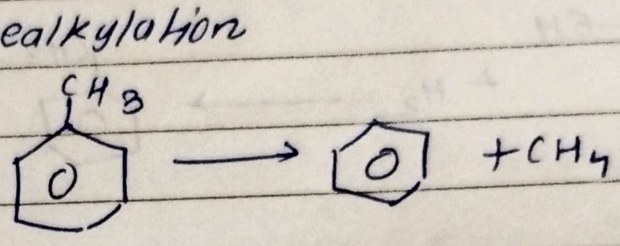
conditions:

$T = 450°C - 500°C$

$P = 10 - 75\ atm$

for low P ⇒ Coke deposition on catalyst
(below 10 atm)

for $P > 75\ atm$ ⇒ Dealkylation



for $T > 500°C$

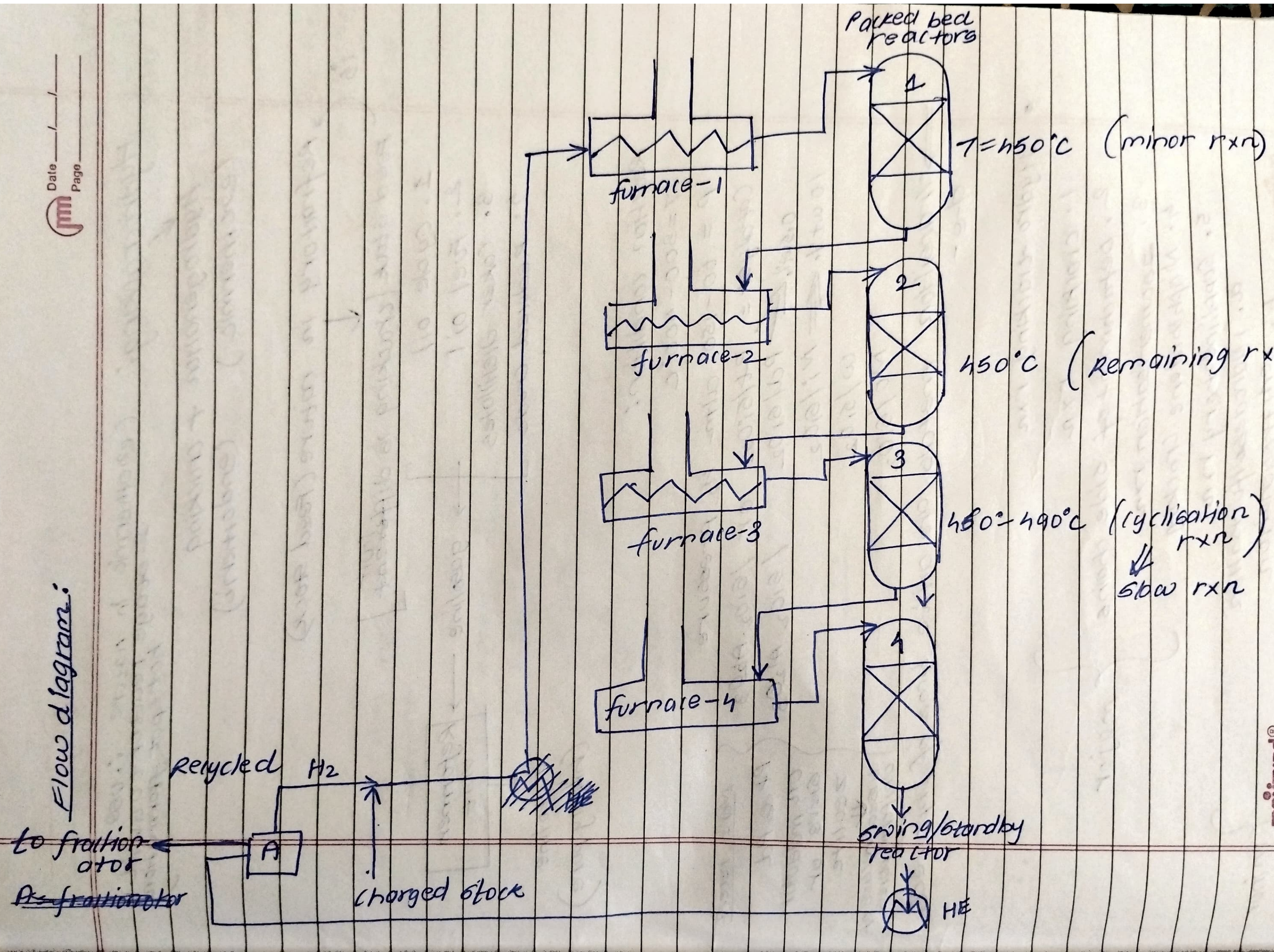
C—C—C—C + C=C—C—C
alkane alkene

↓ Cracking

C (amorphous carbon)

[Coke deposition]

Flow diagram:



Hydrocracking: (endothermic in nature ∴ use 2 stage reactor to avoid hot spot formation)

↓

Hydrogenation + cracking
(exothermic) (endothermic)

is { Refractory in nature (Feed stock)
↓
Feed stock [cracking is difficult]

1. Cycle oil
2. Fuel oil
3. Coker distillates
4. Reduced crude

→ gasoline → $\boxed{\text{Reformer unit}}$ → Gasoline (highly pure)

Reaction condition:

$T = 300-400°C$

$P = 60-150$ atm H_2 pressure

Catalyst = Pt/SiO_2 or $/SiO_2 \cdot Al_2O_3$

0.5wt% ⇐ Pd/SiO_2 $/SiO_2 \cdot Al_2O_3$

10 wt% ⇐ Ni/SiO_2

W/SiO_2

MO/SiO_2

More recent: Pt & Pd on molecular sieve or zeolite ⇓ used becaus of uniform pores size

⟹ Transition metals are active bcoz of unpaired d-e-

- Hydro-cracking rxn

1. cracking rxn
2. Detachment of side chains
3. Isomerisation rxn
4. Naphthalene cracking

} major

5. Supplimentory rxn.
   a. Hydrodesulfurisation
   b. Denitrogenation
   c. Deoxidation
   d. Elimination
   e. Dechlorination

} minor

8/11/23

Hydro-Cracking

Characteristics of catalyst → Acidic sites (enhances cracking) → determined by NH_3 TPD

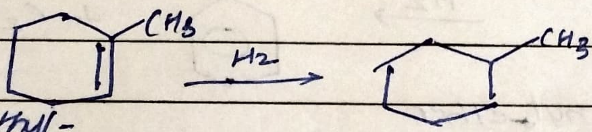
→ Metallic bonds (enhances hydrogenation) → for H_2 chemisorption.

bonds b/w active metal and support

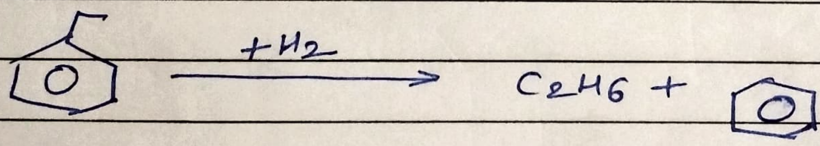
⇒ In both major and minor rxn H_2 is required as reactant.

1. Cracking: a) n-paraffins $\xrightarrow[100\,atm\,P]{H_2}$ Alkane + Alkene.

b) $C_nH_{2n} \xrightarrow{H_2} C_nH_{2n+2}$

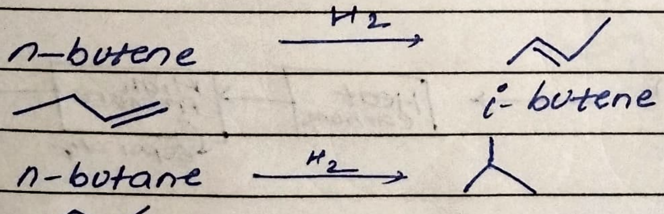
c) 

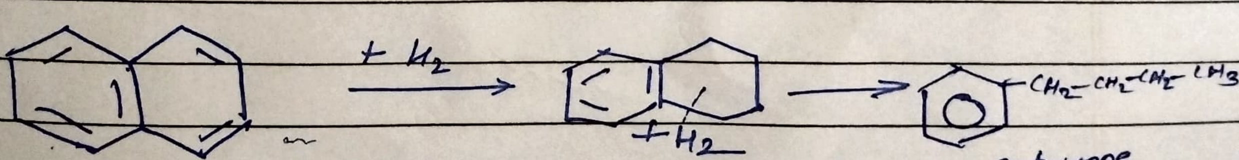
methyl-cyclohexene → methyl-cyclohexane

2. 

3. n-butene $\xrightarrow{H_2}$ i-butene

n-butane $\xrightarrow{H_2}$

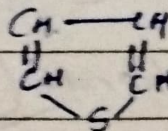


4. 

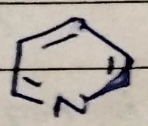
Naphthalene

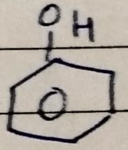
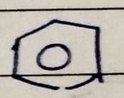
n-butane benzene

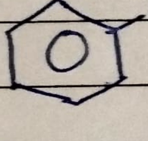
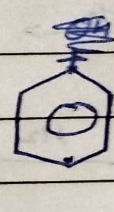
5.

(a)  $+ H_2 \longrightarrow C_4H_{10} + H_2S \uparrow$

$R-SH + H_2 \longrightarrow RH + H_2S \uparrow$

(b)  $+ H_2 \longrightarrow C_5H_{12} + NH_3 \uparrow$

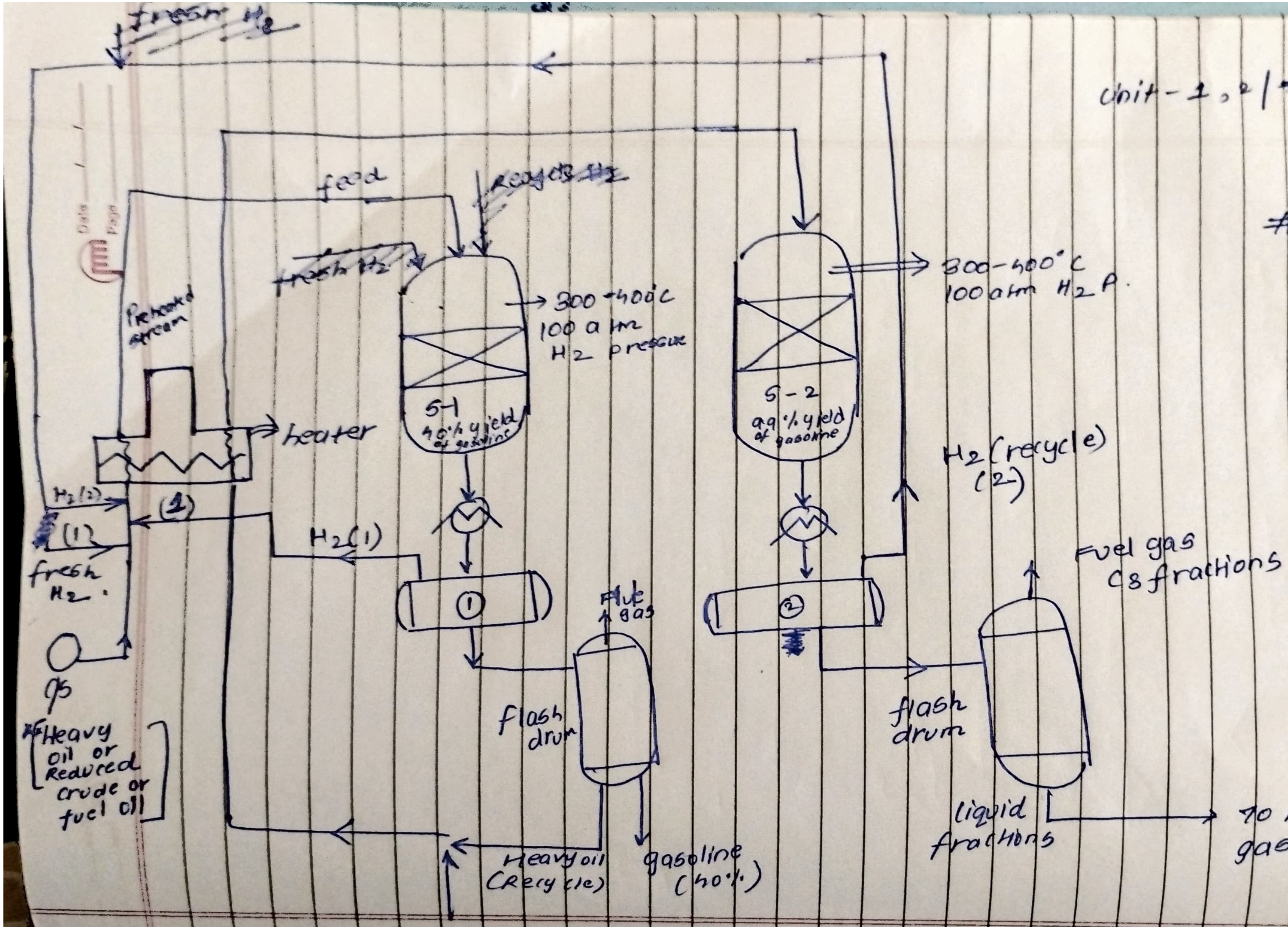
(c)  $+ H_2 \longrightarrow$  $+ H_2O\,(g) \uparrow$

(d)  $\xrightarrow{H_2}$  $+ C_2H_6 + H_2O$

Benzyl-ethyl ether

(e) $R-Cl \xrightarrow{+H_2} RH + HCl\,(g) \uparrow$

effluent stream $+ H_2$ $\longrightarrow$ $\boxed{\text{Heat exchange}}$ $\longrightarrow$ $\boxed{\text{High Pressure Seperator}}$ $\longrightarrow$ H_2 Recycle



Unit-1, 2 |→ high pressure separator

Catalyst

Pt/SiO$_2$ in pellet diameter = 8mm

(1) ⇒ associated with stage 1

(2) ⇒ associated with stage 2.