

Gross Calorific Value:- Represents the total heat released when a fuel is completely burned.

It includes the latent heat of vaporisation of water formed during combustion of the fuel

$$GCV = \frac{(\text{heat of combustion of dry products} + \text{latent heat of vaporization})}{\text{mass of fuel}}$$

Net Calorific Value : Represents the amount of heat when fuel is burned completely assuming that the vapor formed during combustion remains in gaseous state and doesn't release its latent heat.

$$NCV = \frac{\text{Heat of combustion of dry products}}{\text{mass of fuel}}$$

7th Aug, CPT, Prof. SS

● Basis of Coal

1) Run of mine Coal (R.O.M) :- coal which is extracted out of mine.

2) As Receive Coal :- After extraction the coal is loaded on tracks and taken it at Processing Point. During this point of conveying the properties of coal gets changed. This is known as.

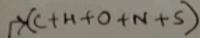
3) Air dried :- During transportation, coal may get dried (moisture content may get changed).

4) Dry Coal :- subtract moisture content and make the rest to 100%.

5) Dry and ash free (d.a.f.) :- remove moisture content, ash from the and take % of the rest contents. That is ...

6) Dry and mineral matter free (d.m.m.f.):

7) moist-mineral matter free / mineral matter free:



### Coal Combustion

- doesn't depend on characteristics property of coal.
- depends on conc. of fuel compound.
- Oxygen content of coal decreases with the rank of coal.
- Volatile matter content - - - - -
- Fixed carbon content increases - - - - -
- Bituminous coal has highest calorific value.

### Action of heat on coal:-

- devolatilisation:
  - active devolatilisation: oil come along with vapours.
  - It involves emission of volatile gaseous matter
- for peat and lignite start decomposing at around  $100^{\circ}\text{C}$ .
- for bituminous coal  $200-300^{\circ}\text{C}$ .
- Active devolatilisation of bituminous coal starts at  $300-375^{\circ}\text{C}$ .
- For bituminous coal, Primary devolatilisation starts at  $350-550^{\circ}\text{C}$ .  
Products obtained  $\rightarrow$  Pyrolytic water, Primary tar and gases (hydrocarbon gases)  $\downarrow$   
secondary devolatilisation starts at  $700^{\circ}\text{C}$ .  
Products  $\rightarrow$   $\text{H}_2$ , secondary tar, lower hydrocarbon gases like  $\text{CH}_4$ .  
 $\downarrow$  Pitch

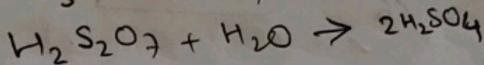
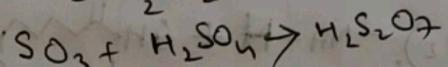
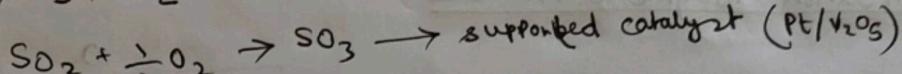
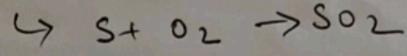
# Peat and lignite only shows primary de-volatilisation.

8/08/23 / Prof. B.B.

## H<sub>2</sub>SO<sub>4</sub> manufacturing

i) Chamber Process

ii) Contact Process



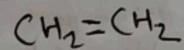
P.E.

Monomeric Unit

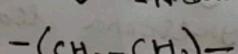
↓  
Dimer

↓  
Trimer

↓  
Tetramer  
↓  
Polymer



Monomeric unit  
↓  
60-100 atm, 70°C  
Zn catalyst



n = no. of repeat unit

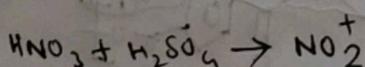
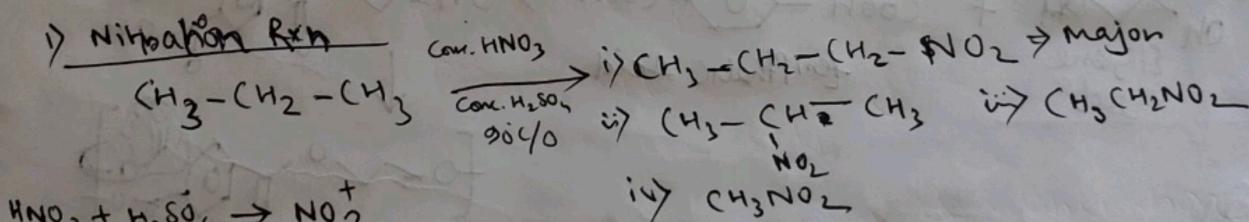
Z.N. Catalyst

Zigler-Natta catalyst

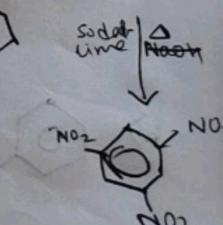
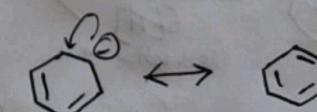
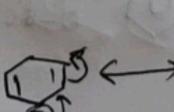
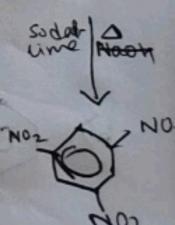
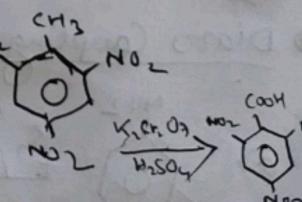
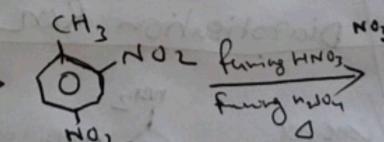
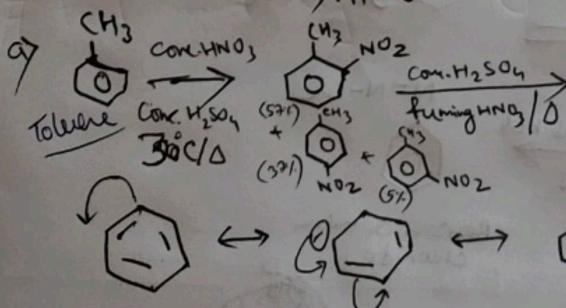
Tidyl + Al  $\leftarrow$  C<sub>2</sub>H<sub>5</sub>

C<sub>2</sub>H<sub>5</sub>

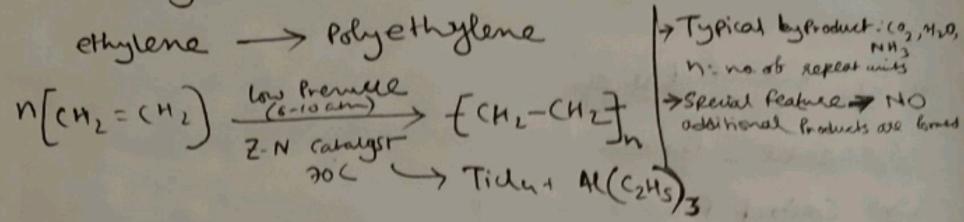
## Nitration Rxn



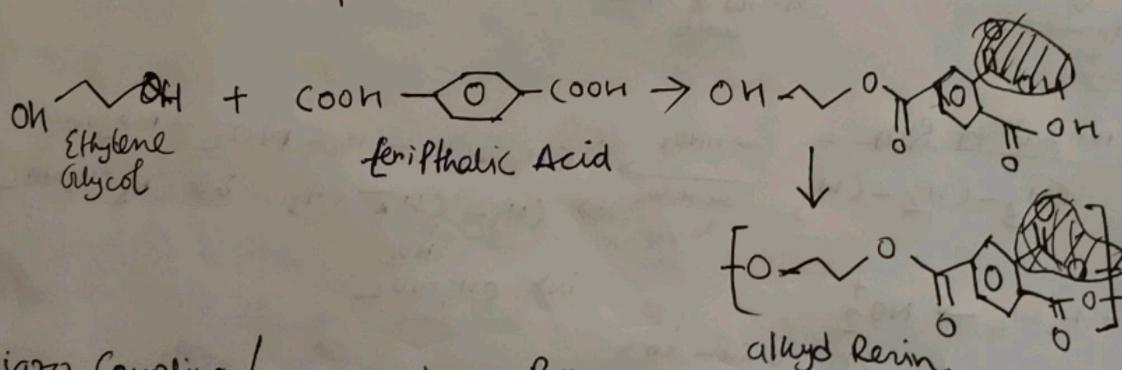
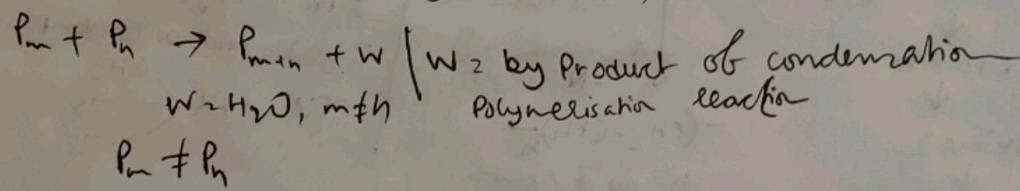
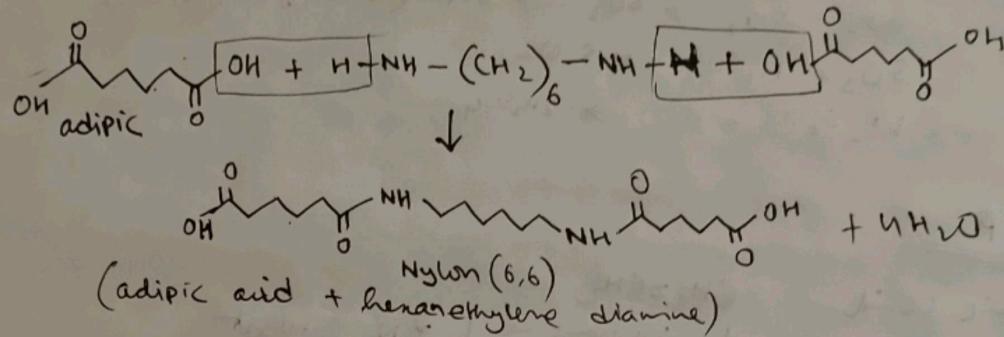
nitronium ion



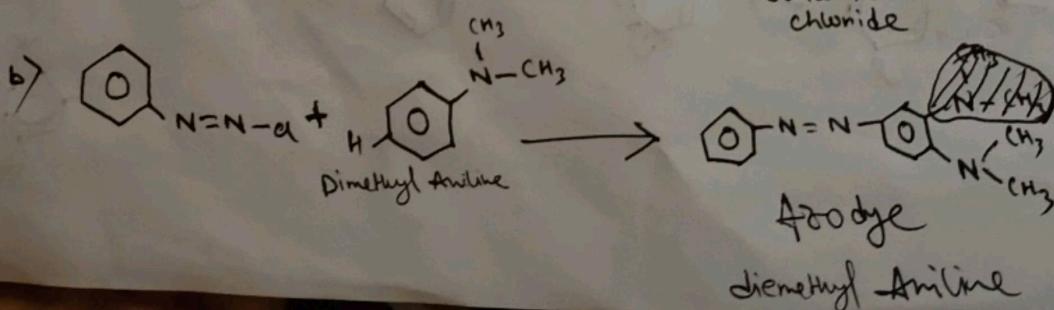
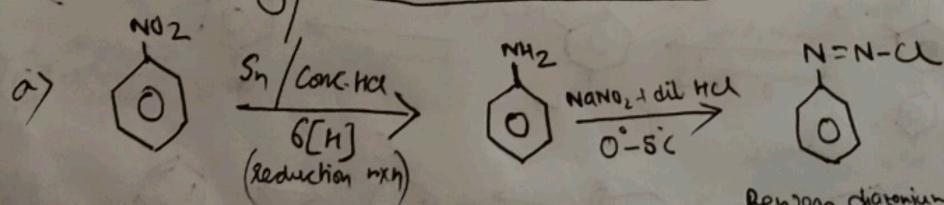
### Additional Polymerisation



### Condensation Polymerisation



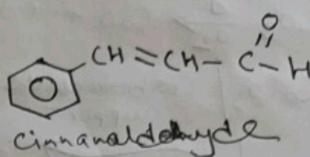
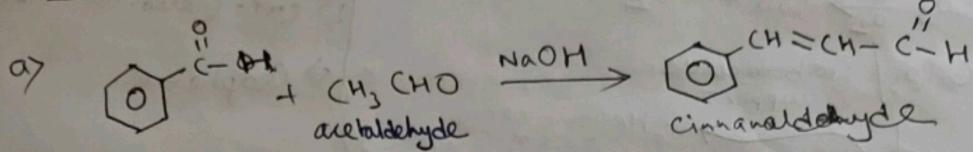
### Diazo Coupling / Diazotisation Rxn



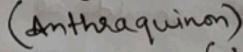
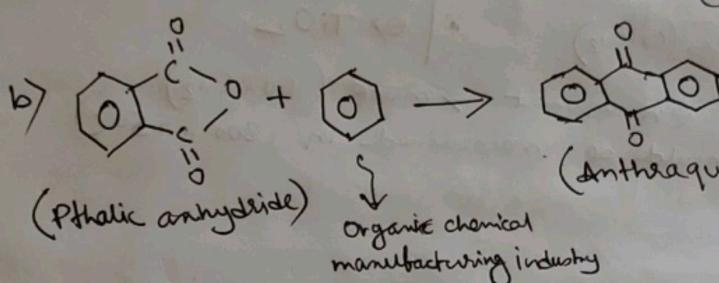
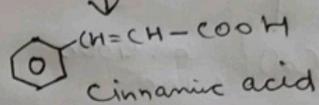
This reaction is used in dye manufacturing industries.

### Condensation Reaction

Product:  $\text{CO}_2, \text{H}_2\text{O}$ ,  
NH<sub>3</sub>  
heat units  
 $\Rightarrow$  NO  
products are formed

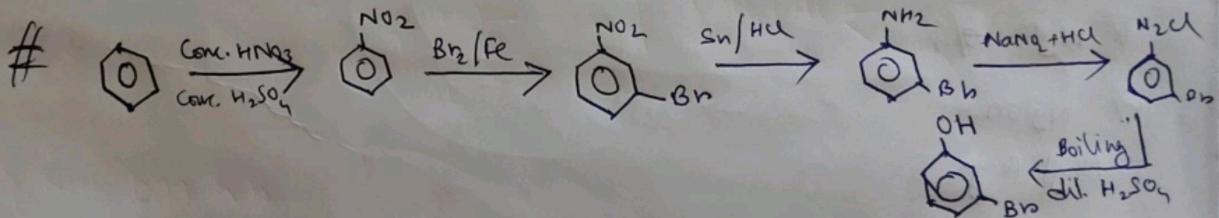
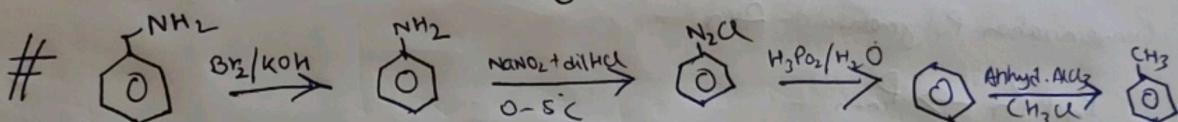


$\downarrow [\text{O}]$

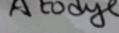
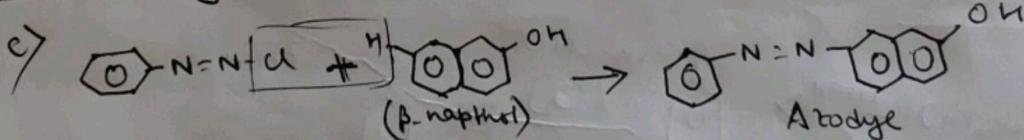


Organic chemical  
manufacturing industry

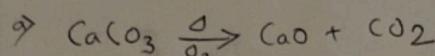
Paper and pulp  
manufacturing industry



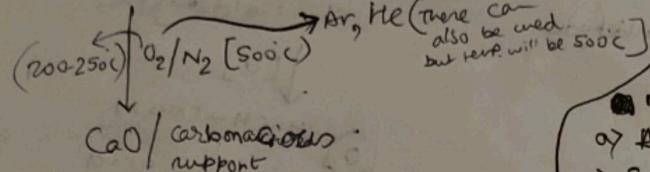
### Diazo coupling



### Calcination / Decomposition Rxn



b)  $\text{CaCO}_3$  / Carbonaceous support



CaO / carbonaceous support

In case of  $\text{N}_2 \rightarrow \text{len}(\text{CO} + \text{CO}_2)$ .

In case of  $\text{O}_2$ , environment  $\rightarrow$  more  $(\text{CO} + \text{CO}_2)$ .

So, rxn temp. should be maintained in (200 - 250°C).

Carbonaceous supports —

a) Activated Carbon

b) CNTs (carbon nano tube)

c) Graphene

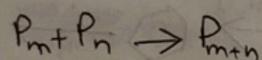
Non-carbonaceous supports —

a)  $\text{Al}_2\text{O}_3$  b)  $\text{SiO}_2$ ,

c)  $\text{SiO}_2 - \text{Al}_2\text{O}_3$  d)  $\text{ZnO}_2$

e)  $\text{TiO}_2$

### Condensation Polymerisation Rxn:

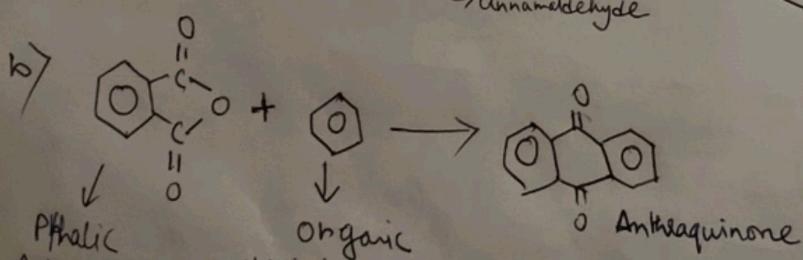
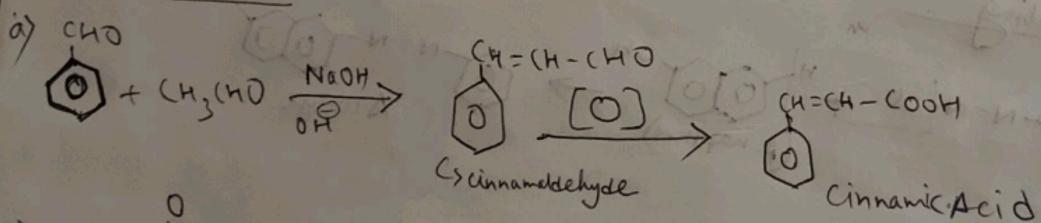


↳ Nylon 6/6

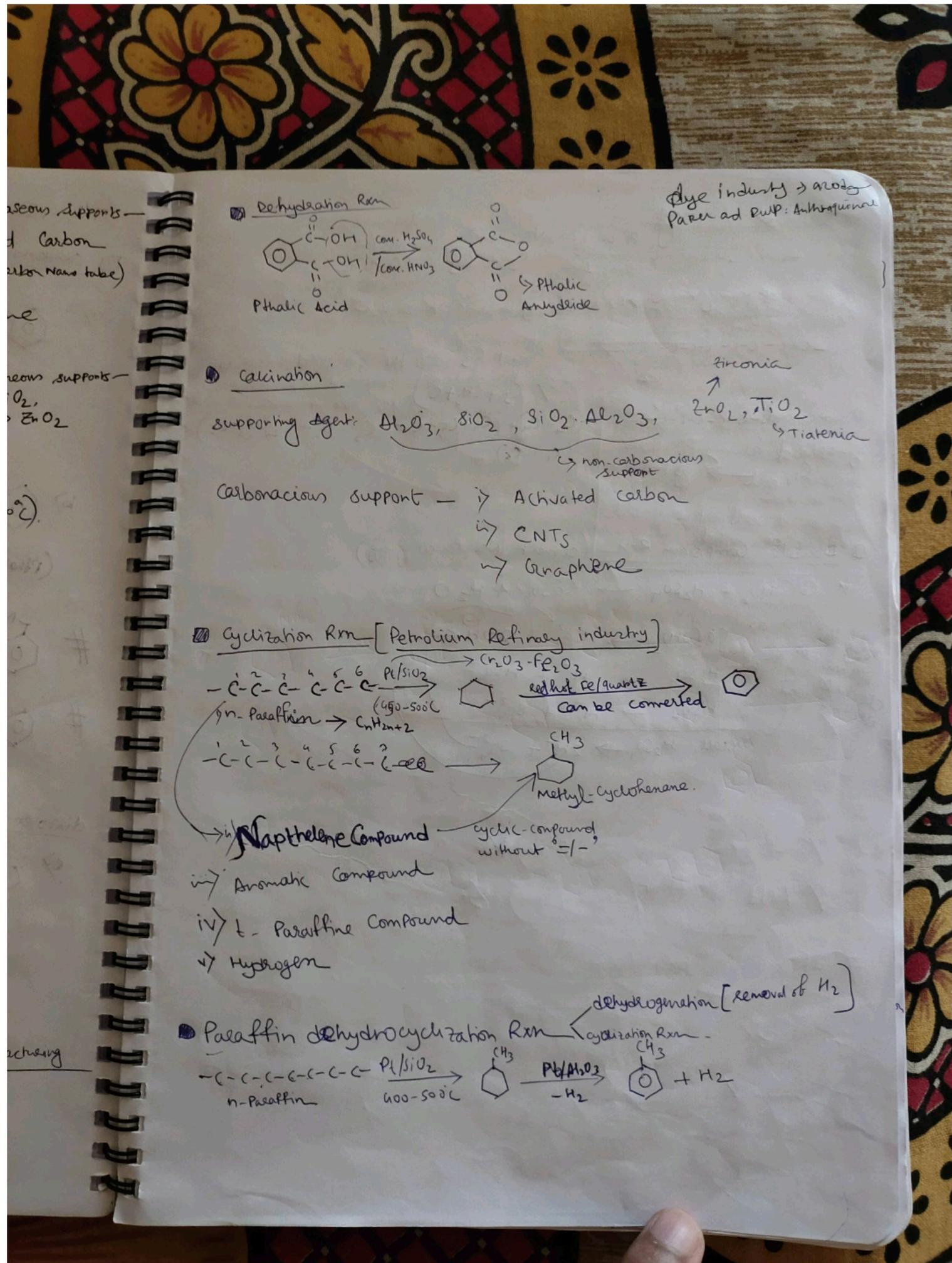
↳ Nylon 6

↳ Alkyl Resin

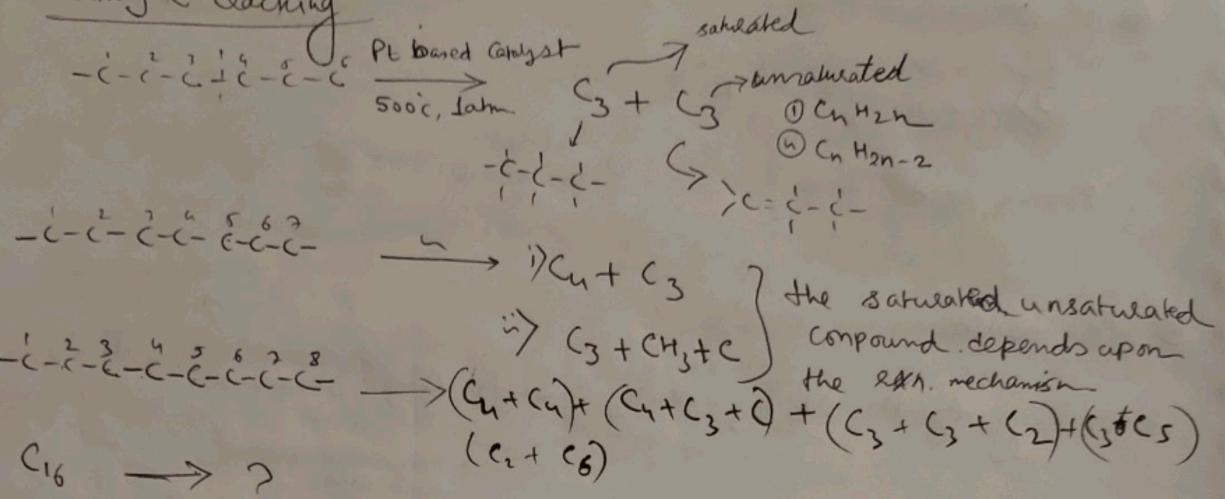
### Condensation Rxn



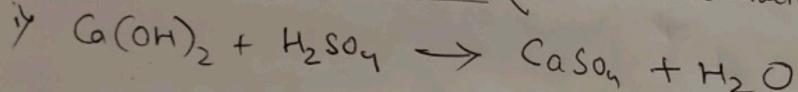
↳ Paper and pulp manufacturing industries.



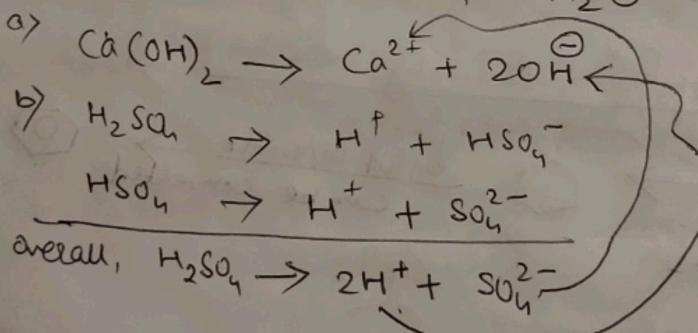
• Catalytic Cracking



• Double Composition Rxn (cement manufacturing eng.)



why the name is  
double decomposition



bonding stability

14th Aug  
Prob. SS

### • Coal Preparation

→ size reduction Simplest Operation → Separation of fines from the lumps.  
(Smaller industry)

For larger plants → various operations includes —

- i) size reduction
- ii) size separation [use screen] → Revolving Screen, Vibrating Screen, Shaking Screen
- iii) Cleaning
- iv) drying
- v) mixing

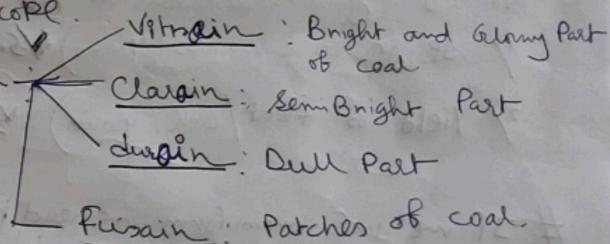
After these methods, hand picking method is used to remove the visible darts.

Large Coal is consist of two parts —

- a) dull coal: - Preferred for furnace and boilers
- b) Bright coal: - domestic use and coke preparation.

# Coal Petrography: - Petrography = Study of differentiating coal components by visual method, with or without the help of microscope.

Macroscopic Characteristic of Coal



Vitrain: Bright and Glowing Part of coal

Clarain: Semi-Bright Part

Durain: Dull Part

Fusain: Patches of coal.

### # Float and Sink Test

(Washability method measurement)

- i) Total Float-ash curve → Yield of clean coal (float) v/s. its ash content
- ii) n Sink-ash → n n refuge (sink) v/s its ash content
- iii) Washability Characteristics Curve. → How far it is possible to separate the dust from the clean coal by washing.

→ Solvents used for washing: Mixtures of various organic liquids  
Benzene (sp. gr. 0.88), Toluene (sp. gravity 0.87),

CCl<sub>4</sub> (sp. Gravity 1.6), Bromoform (2.9)

# Solvent sp. gravity range → 1.2 to 1.6 by increment of 0.05.

# Float and Sink Test:  
Weighted Portion of Coal      Treated with SP gravity 1.2

float on top surface } air dried, weighed,  
Sink at bottom      } ash and moisture content are determined separately at each step.

### Float and Sink Method

→ Applied to any Particle size of coal, usually 1-2 inch screen size.  
→ Air dried coal not very coal should be used.

Treated with solvent of sp. gp 1.25

↓ float

sink

Treat with solvent of next sp. gp.

Continued

Washing with solvent with sp. gp 1.6

### Mineral Matter of Coal

1) Inherent Matter: moisture content,

2) Extraneous Matter: Mudstone, siltstone

→ Coal wash is effective for these as they can be removed easily.

### # Washability characterisation of coal

1) sp. gr. of solvents (Y axis) vs. ash content of floats (X axis) or sinks

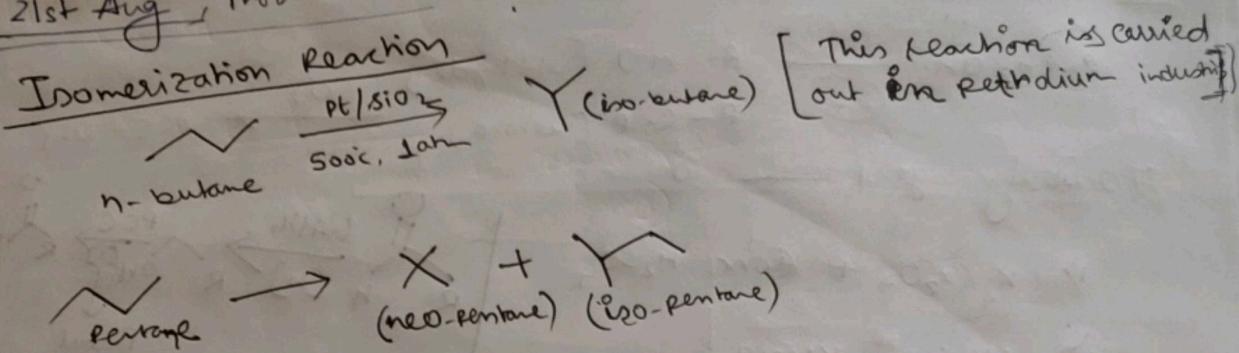
2) Yield of float/sink (Y axis) vs. ash content of float/sink (X axis)

# If we use bromoform, we need to wash the float and sink with methyl alcohol to remove bromoform so as to make it easier to air dry the content.

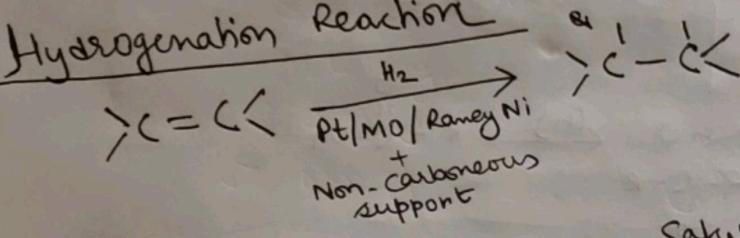
It is not easy to evaporate bromoform.

21st Aug, Prob B.B.

Isomerization Reaction

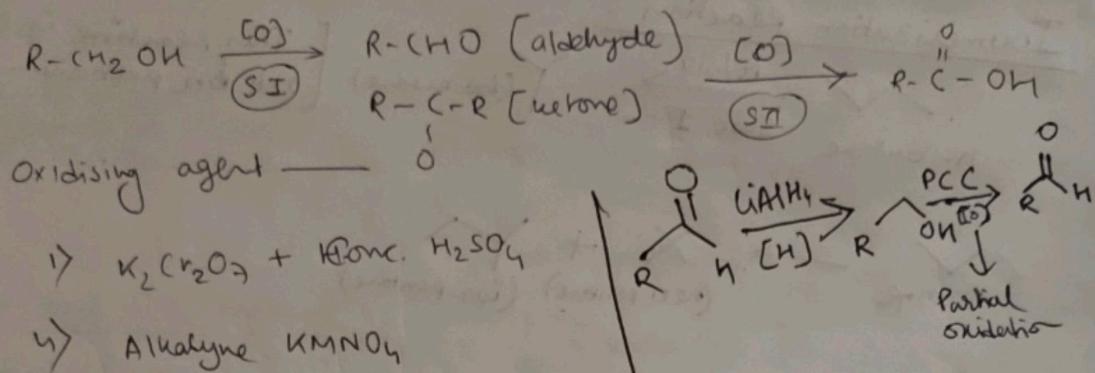


Hydrogenation Reaction

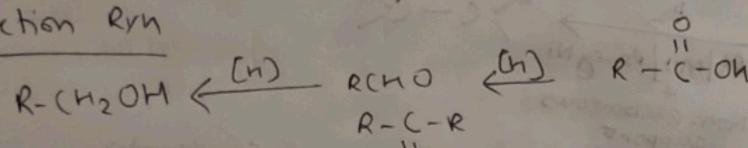


Basically, unsaturated  $\rightarrow$  Saturated Compounds  
(Paraffins)

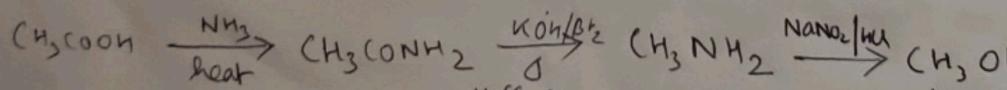
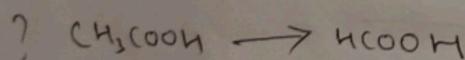
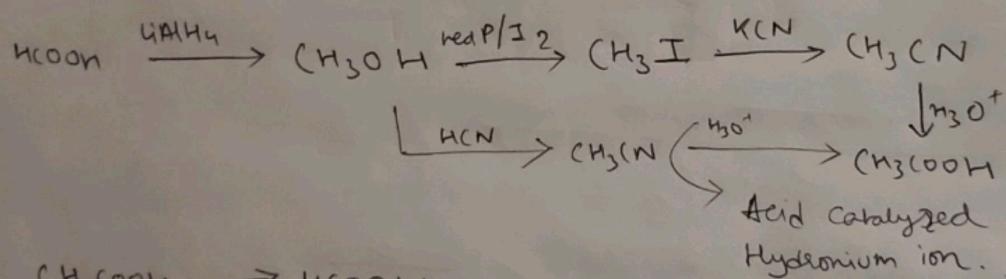
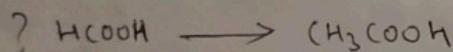
## Oxidised Rxn



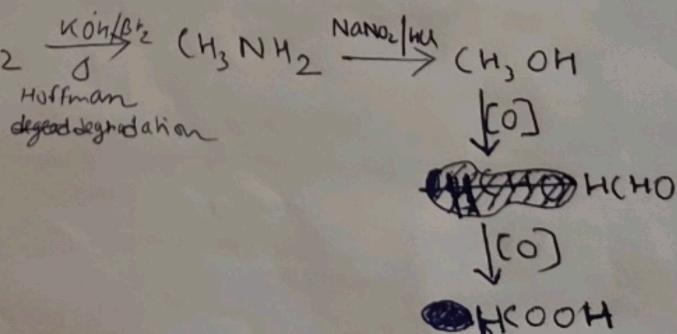
Reduction Ryn



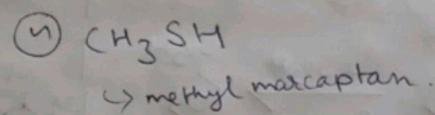
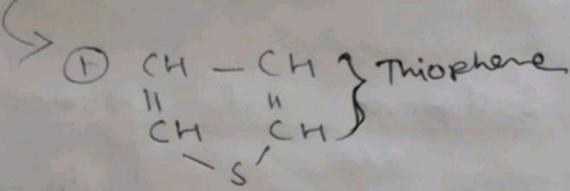
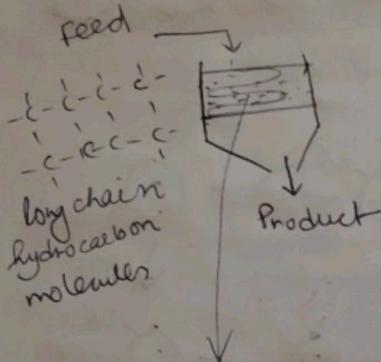
Reducing Agent = LiAlH<sub>4</sub>



Huffman  
degradation



# Hydrolytic Hydrodesulfurization Rxn  
 Removal of sulphur compounds.

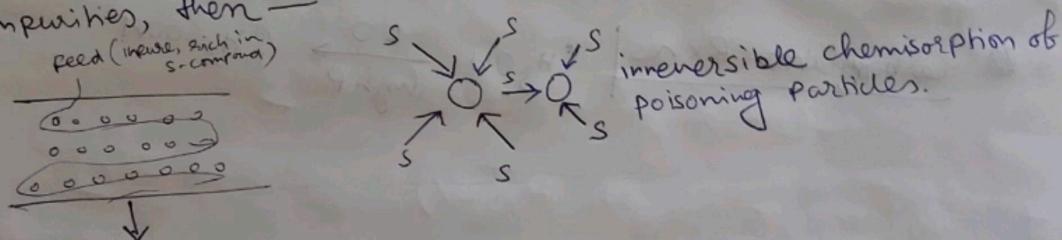


If there is powder form in fixed bed —

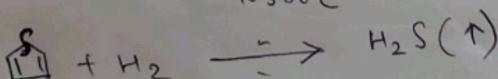
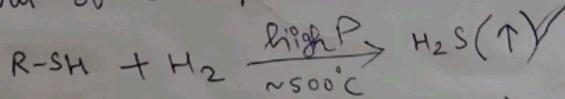
Product will be  $\Rightarrow$  Product + Catalyst + unconverted feed.

But if the fixed bed is pellet ( $\sim 3\text{mm diameter}$ ), then we will get only Product.

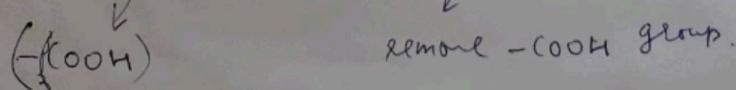
Now, if feed is not pure and contain S-compounds as impurities, then —



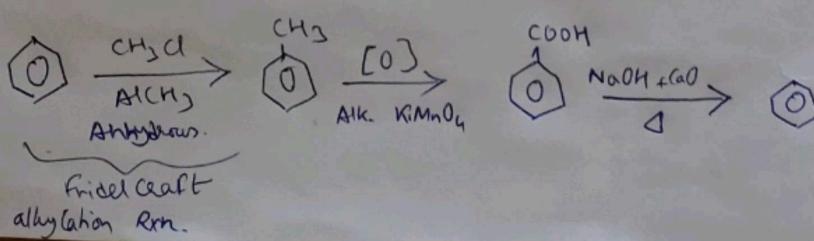
Removal of S-compounds —

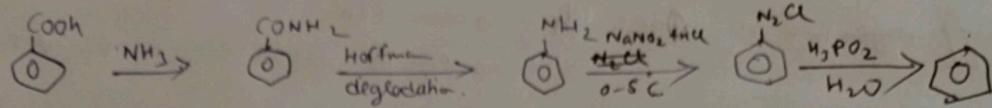


# Carbonylation and Decarbonylation Rxn

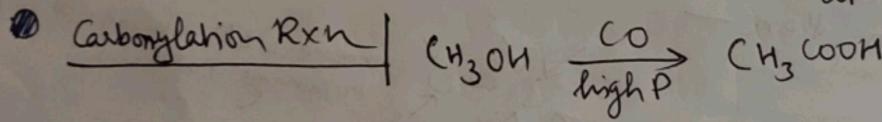
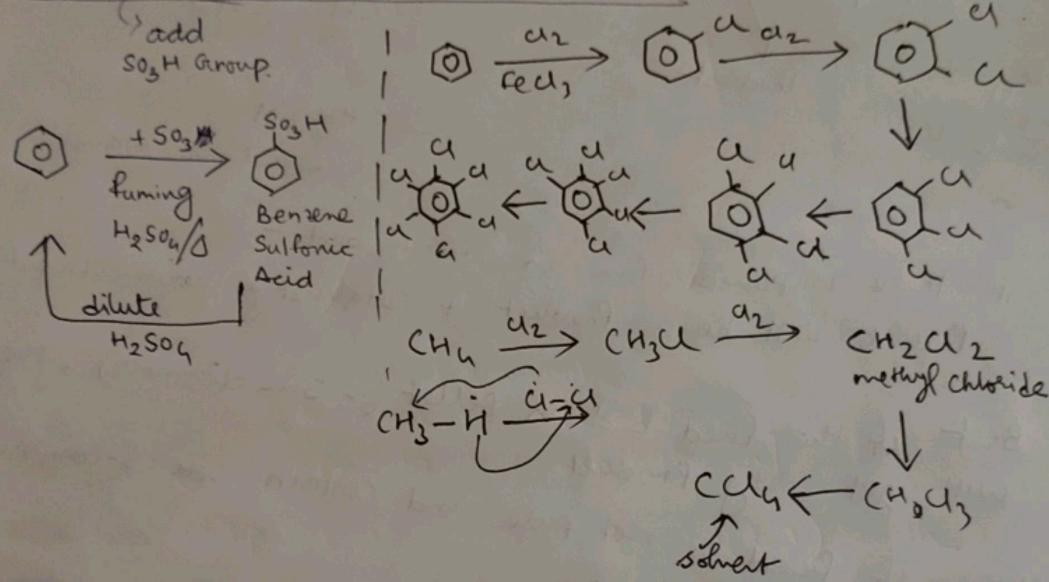


[Organic chemicals manufacturing industries make use of carbonylation and decarbonylation rxn.]





### # Sulfonation and Chlorination Rxn



21st Aug, Prob. SS

## Recovery of Clean Coal

$$\% \text{ recovery} = \frac{\% \text{ ash in refuse} - \% \text{ ash in feed}}{\% \text{ ash in refuse} - \% \text{ ash in clean coal}} \times 100$$

# Extent of carbonisation: % of volatile matter present.  
 Ash and P → Concentrated in coke  
 S → remaining unchanged

Coal Carbonisation: heating coal at high temp (absence of air) to form coker coal which has higher calorific value than the parent coal.

i) Low temp carbonisation (LTC) at around  $600^{\circ}\text{C}$

ii) Med. - (MTC) - -  $800^{\circ}\text{C}$

iii) High - (HTC) - -  $1000-1100^{\circ}\text{C}$

Process occurs at lower temp and product formed is soft coke / semi coke / briquette / char. smokeless domestic fuel.

Major Product → coke + coal gas.

→ Not practised commercially. Mostly LTC and HTC is operated commercially.

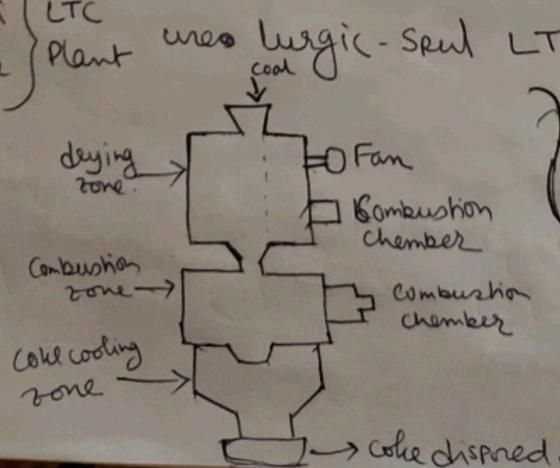
# In semi-coke, coal comp. are more conc., so calorific value is high, that is purpose of carbonisation.

→ Leco (name of semi-coal they prepare.)

[ moisture are evaporated + solidified ]

Nayveli { LTC

Naspur } Plant uses Burgie-Spat



LTC Process.

→ While taking through vertical shaft, coal is successively dried and carbonised

Burgie-Spat

→ Coal size 25-125 mm

LTC

→ Hot gas remain in drying zone Diagla. by the help of big fan. It is removed by chimney after getting cool.

→ at high temp, coal evolves lot of volatile matter, these produce high valuable products (By). Carbonisation gas shouldn't go to drying zone.



22nd Aug

## Coke Oven

(used for Production  
of coke from coal)

By-Product  
slot type  
(not only produce coke  
but also capture various  
by products)

Heat transfer is by radiation and by conduction from layer  
to layer.

Beehive Coke Oven: The coal from the mines was dumped into the oven through opening at top. The coal is ignited and sealed to remove oxygen. About 70% of coal turned into coke.

By Products are burned in (i) to supply heat of carbonisation, whereas by products are removed in (ii).

# Coke from coke oven → used in metallurgical purpose

Coal gas → Principle use as town gas.

↳ (Coke oven gas)

Retort coke → unsuitable for metallurgical use, but is a good domestic use.

↳ Specialised vessels or chambers used in production of gas from carbonaceous solids.

Gas Retorts → horizontal Retort → used for wood gas production

↳ Intermediate-retile retort

↳ continuous-retile retort

① Demerits of Beehive Coal Oven:-

i) No recovery of by products

ii) lower quality coke due to partial combustion.

iii) lack of flexibility of operation

iv) Production of quality coke only by using good coking coal.

Merits:— i) extremely good quality, strong and blocking coke of req. reactivity is obtained if the starting coal is of good coking quality

ii) low capital and running cost

iii) Coke production is not connected with the availability of a market for the byproducts.

# Coke: Hard, porous, carbonaceous material.

→ source of reactive carbon in blast furnace, gasifiers, boilers.

## Test for Coke Strength or brittleness:-

a) Shatter Test

b) Micum Test

## # Three imp. Properties of Coal :-

Purity	Strength	Reactivity
Moisture, ash, sulphur, phosphorous	hardness/brittleness measured by Shatter, Micum test	→ no standard reaction tests, but porosity may give an indirect measure of reactivity.

Shatter Test:- 4 lines coke is dropped from a height of 6ft over a metal plate. After that it is sieved in 4 types of different sieves. And the hardness is reported as the % of oversize and undersize on specific sieves. Eg. if 80% coke remains intact after the impact, the result is recorded as 80% shatter. Higher shatter values indicates stronger and less brittle coke, which is desirable.

Micum Test:-

Purpose:- to measure the resistance of coke to abrasion and measuring its structural integrity when subjected to mechanical wear. This is particularly important for coke used in transportation and handing systems.

Process:- coke samples are rotated in a metal drum at a definite rate for a set specific period and reported as % oversize, undersize of a specific screen.

# Coke with lower Micum index is preferred for applications where it needs to endure mechanical wear and abrasion without significant detonation.

## ● Coal to Coke Transformation:-

- a) Coal Preparation :
  - Raw materials is mined from source
  - Coal is then cleaned, crushed, sorted to remove impurities
- b) Heating Process :
  - Prepared coal is introduced to coke oven
  - heated in absence of air at 2000°C [Carbonisation]
  - By products are collected
- c) Formation of coke :
  - As coal heated up undergoes physical, chemical changes
  - The remaining carbon rich material solidifies and transforms into coke, high % of carbon
- d) Quenching and Cooling :
  - hot coke is quenched and cooled rapidly to stop carbonisation process.
  - often done by spraying the hot coke with water or another cooling medium.
  - This rapid cooling helps coke from further softening.
- e) Coke sorting and handling
- f) By Product Recovery
- g) Quality Control

● Coal liquification : Adding off or increasing hydrogen content of a coal is called coal liquification. Carbon is called 'carbonisation' just like removing

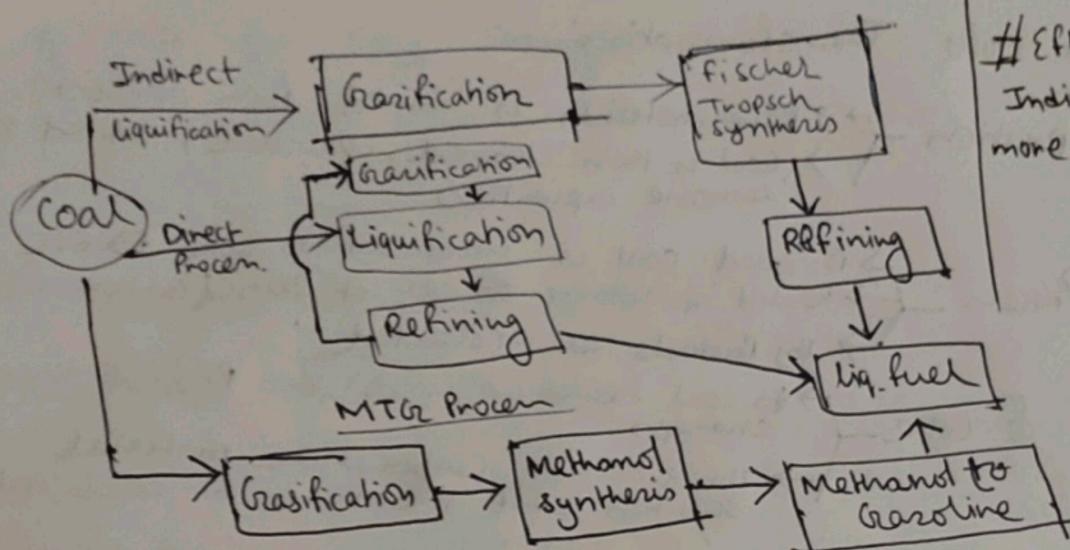
Direct  $\begin{cases} \text{single stage} \\ \text{double stage} \end{cases}$

Coal liquification  $\begin{cases} \text{Indirect} \\ \text{for Coal Liquification plants} \end{cases}$

~~These are three options for Coal Liquification~~  
 $(\text{Hydrogen Content}) > (\text{Hydrogen Content})$   
in lig. coal of solid fuel coal

H.C type lig. fuel obtains by —

- i) hydrogenation of coal [Bargius Process]
- ii) Solvent extraction of coal and hydrogenation of coal extract
- iii) Refining of tar and oil obtained by carbonisation of various solid fuels
- iv) Cracking of solid fuels into synthesis gas and conversion of latter into lig. fuels and chemicals.  
Exmp. Fischer Tropsch Process, MTG (methanol to gasoline) Process.



# Efficiency of Indirect Process is more than direct one.

- Direct Liquification →
  - i) Single Stage → Produces distillates via primary reactions
  - ii) Two Stage → Produces distillates via two reactors in series

Two main key stages —

- i) Hydrogenation: At this 1st stage coal is liquified. The crushed coal is mixed with hydrogen-rich solvent and mixture is subjected to high pressure and temp. conditions. During this —
  - a) coal molecules breakdown into smaller fragments, ~~releasing~~ volatile compounds
  - b) leads to saturation of carbon-carbon and carbon-hydrogen bonds, converting coal's complex str. into simpler one.
  - c) Sulphur, Nitrogen present in coal may also undergo hydrogenation to make the product cleaner and simpler.
- ii) Depolymerization and Hydrocracking: After hydrogenation, resulting mixture still contain complex hydrocarbons. So additional hydrogen is introduced, mix. is further heated and premixed.
  - a) The complex hydrocarbon from first stage break down into smaller, more uniform hydrocarbon.
  - b) High pressure favours cracking of larger molecules into smaller one.
  - c) The goal is to produce liquid hydrocarbons with properties similar to ~~petro~~ petroleum-based crude oil.

29th Aug, B.B.

Pores in support →  
Micro pores ( $< 2\text{nm}$ )  
Meso pores ( $2\text{-}50\text{nm}$ )  
Macro pores ( $> 50\text{nm}$ )  
# BET surface area analysis helps to determine pore diameter

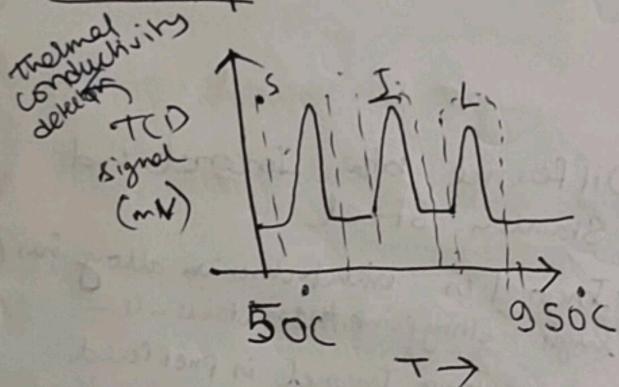
Surface acidity / basicity

Feed:  $\text{CO}_2/\text{H}_2$  (for surface basicity measurement)

Feed / Probe gas ( $\text{NH}_3/\text{H}_2$ ) for surface acidity measurement

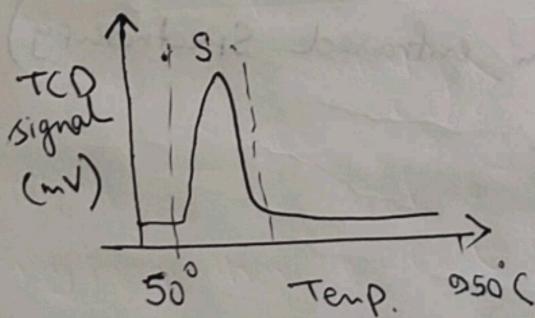
- low T → strong acidic functional groups.
- Intermediate T → Intermediate acidic func' groups.
- High T → low acidic functional groups.

Cae-I | Existence Extent of S.I., Low acidic functional groups.

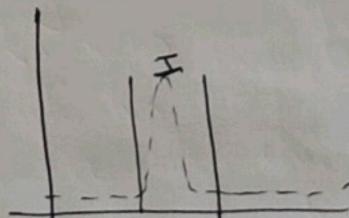


Cae-II

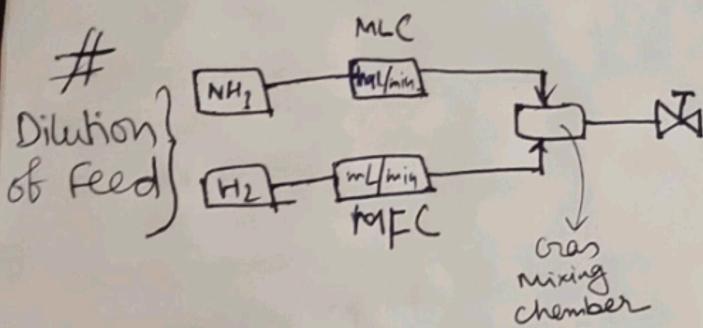
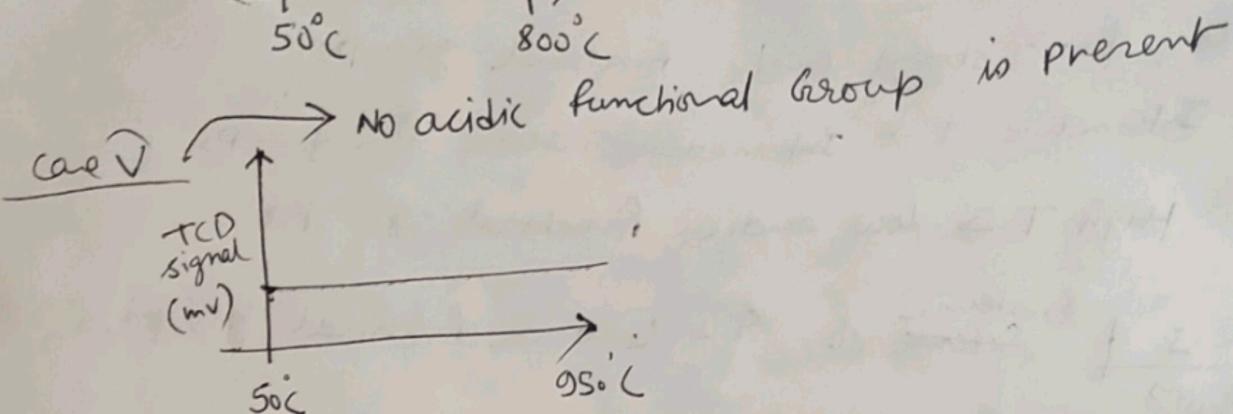
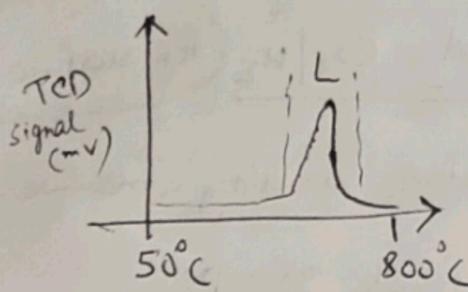
Existence of Strong acidic func. group.



Cae III → Instantaneous Intermediate acidic func group (only)



Case - IV : Weak acidic functional group.

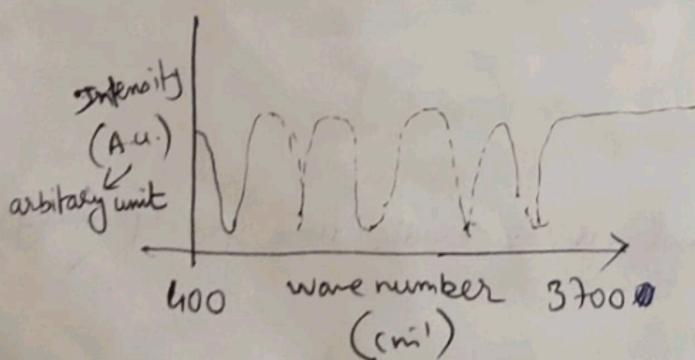


Difference b/w. Inconel and Stainles Steel

- Inconel is nickel-chromium alloy has high melting point, then stainles steel.
- At high temp Inconel is preferred and low temp. stainles steel is preferred.

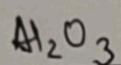
④ Determination of functional Groups.

⇒ FTIR (Fourier Transform infrared Spectroscopy)



## Preparation of Catalyst (Heterogeneous) | $\text{NH}_4\text{VO}_4$

Support (99.99% Pure)

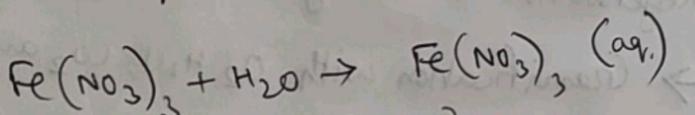


Next step → Incorporation of active metal/metal oxide

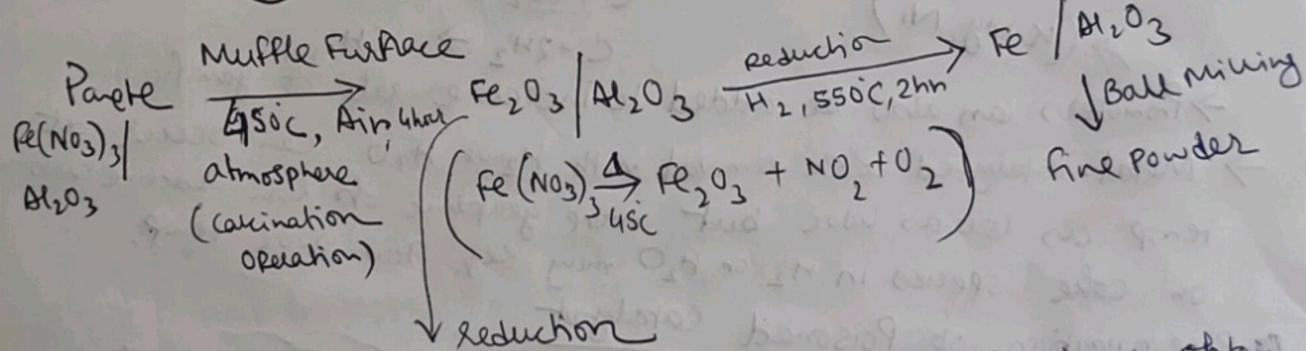
Precursor Salts :-  $\text{Fe}(\text{NO}_3)_3 \xrightarrow{\text{2H}_2\text{O}} \text{FeSO}_4 \xrightarrow{\text{Acetate}} \text{Fe-Acetate}$

req. to form catalyst  
when  $\text{Al}_2\text{O}_3$  is mixed with say Fe, catalyst don't form.

Now,  $\text{Fe}_2\text{O}_3 \mid \text{Al}_2\text{O}_3 (\text{fg})$  = objective



Now,  $\text{Fe}(\text{NO}_3)_3 \xrightarrow{\text{dropwise}} \text{Al}_2\text{O}_3 \Rightarrow \text{Parte will form.}$



Reduction  $\xrightarrow{\text{Gas Phase (reed: } \text{H}_2 / \text{CO}_2 / \text{H}_2 + \text{CO}_2\text{)}} [\text{motto is to obtain } \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}]$

Liquid Phase  $[(\text{NH}_2)_2\text{NH}_2 \cdot \text{H}_2\text{O} / \text{NaBH}_4 / \text{Citric acid}]$  (motto is same).  
 $\downarrow \text{hydrazine mono-hydrate}$

$\text{Fe}_2\text{O}_3 / \text{Al}_2\text{O}_3$  (Fine Powder)  $\xrightarrow[\text{550}^\circ\text{C, 2 hour}]{\text{Reduction, } + \text{H}_2} \boxed{\text{Fe} / \text{Al}_2\text{O}_3} \xrightarrow{\text{Ball milling}} \text{fine Powder}$

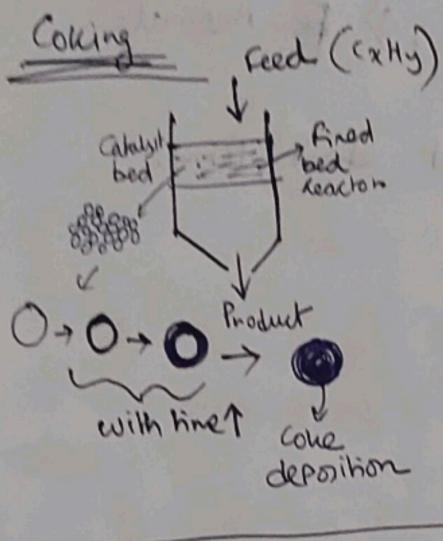
if we use  $\text{Ag/SiO}_2$ , salt :-  $\text{AgNO}_3, \text{AgSIO}_4$   
 $\downarrow \text{Cu, qy : Cu}(\text{NO}_3)_2,$

## # Deactivation of Catalyst —

↳ Coking

↳ Sintering  $\rightarrow$  Narrowing of Pores

↳ Poisoning.

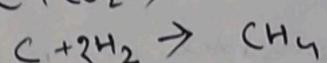
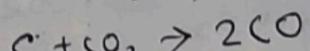
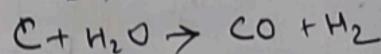


## Regeneration of Catalyst

The ability to reactivate a catalyst process depends on the reversibility of deactivation process.

• Regeneration of catalyst deactivated via Coking —

$\rightarrow$  Granification with  $O_2$ ,  $H_2O$ ,  $CO_2$  and  $H_2$



$\rightarrow (K, Mg, Ni)$

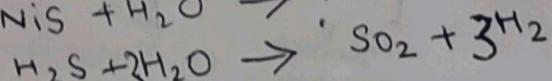
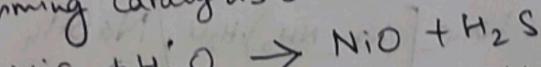
$\rightarrow$  Promoters can also be added to increase rate of granification

$\rightarrow$  Metal-catalyzed coke removal with  $H_2$  or  $H_2O$  can occur at temp as low as  $400^\circ C$  but more graphic of less reactive carbons on coke species in  $H_2$  or  $H_2O$  may req.  $700-900^\circ C$  temp.

• Regeneration of Poisoned Catalyst

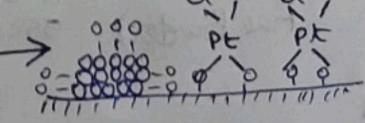
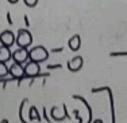
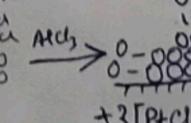
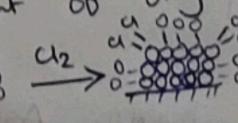
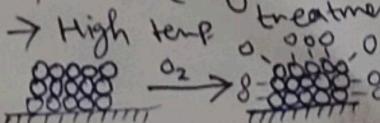
$\rightarrow$  Treatment with  $O_2$  at low pressure and steam at ~~700-900~~  $700-900^\circ C$ .

$\rightarrow$  80% removal of surface sulphur from Mg- and Ca-promoted Ni steam reforming catalysts occurs at  $700^\circ C$  in steam.



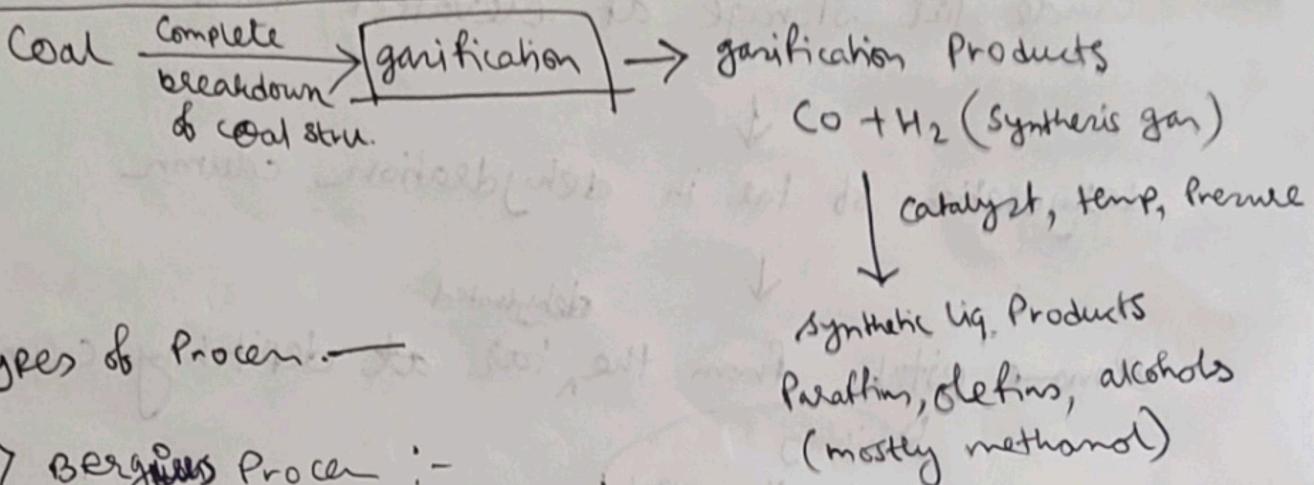
• Redispersion of Sintered Catalyst:

$\rightarrow$  Sintering is very hard to reverse. A mechanism for Pt redispersion by oxygen and chlorine.



Prob. SS, 4th Aug Sep. | end of Coal Industry

## Indirect Coal Liquification :-



Types of Process:-

i) Bergius Process :-

ii) Fischer Tropsch Process: Fossil  $\xrightarrow{\text{gasification}}$  Syn Cras  $\xrightarrow[\text{catalyst } (\text{Co}, \text{Fe}, \text{Ru}, \text{Ni})]{\text{Fischer-Tropsch}}$  light hydrocarbons  
 $\downarrow$  gasoline, diesel

iii) low temp carbonisation: Coal to tar production.

# Tar acids are mix. of various kind of phenols, group of cresols, xylenols along with the aliphatic group.

Tyres  $\xrightarrow{\text{group of Phenol}}$  crude Phenol  
of Tar acids  $\xrightarrow{\text{group of Cresol}}$  crude Cresol  
 $\xrightarrow{\text{group of Xylenol}}$  crude Xylenol

HBTA (High Boiling Tar Acid): unsaturated, big molecule

Crude Phenol,

Tar acids are valuable and can be converted to other chemicals after refining.

Tar distillation plant to recover core chemicals from Tar acids.

Produce tar acid from crude tar  
recovery of ammoniacal liquor  
from coal carbonisation plant.

# ⇒ TDP (Tar Distillation Plant)

\* Crude Tar storage at elevated Temp.

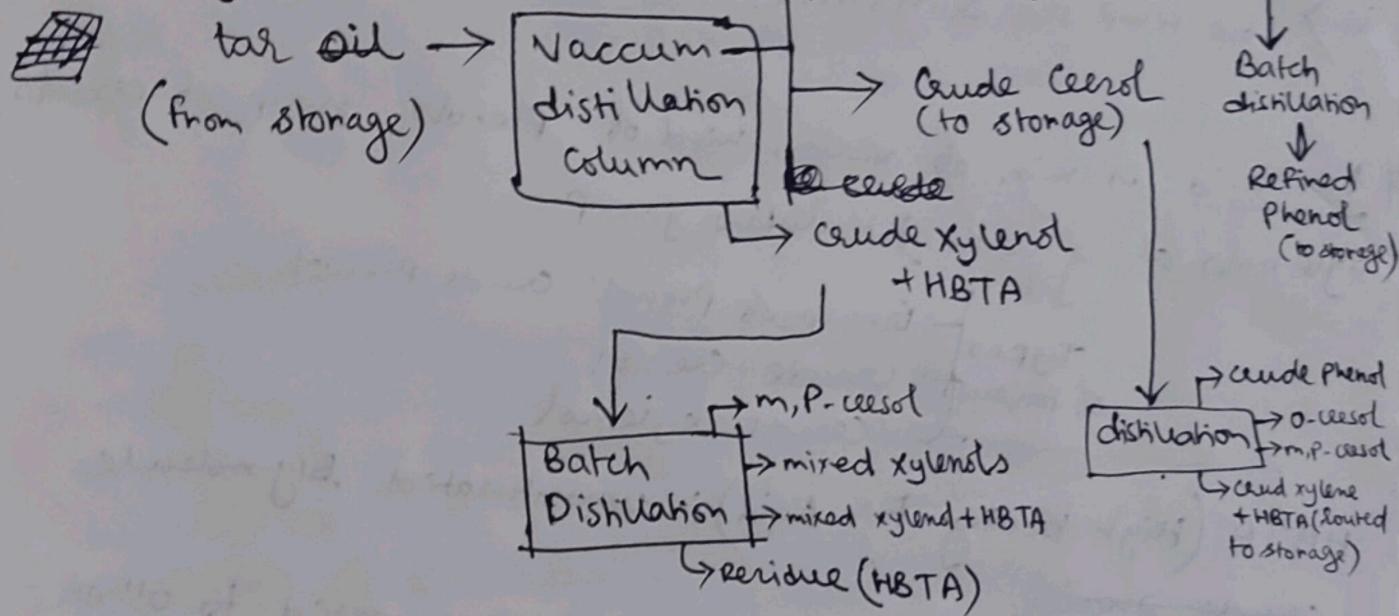
↓  
dehydration of tar in dehydration column

↓  
remove 'pitch' from the tar at depitching column

(highly  
carbonaceous pdt.)

↓  
separate tar oil in fractionating column  
(contains tar acids)

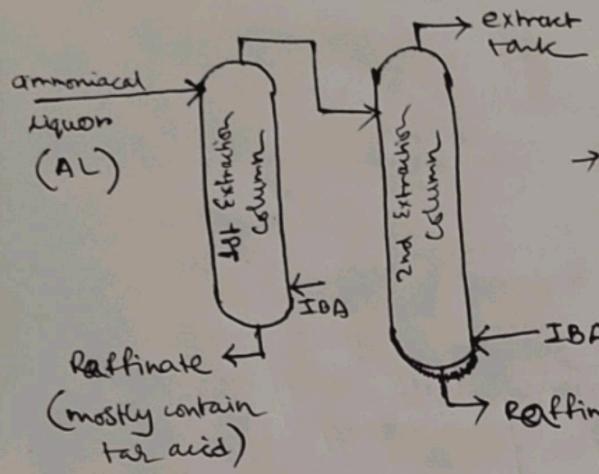
## ⇒ Recovery of Tar Acid



## ② Ammoniacal liqu. Extraction Section

Purpose: to extract tar acids in the ammoniacal liquor  
Using the solvent isobutyl alcohol (IBA)

→ is done in two stage extraction column



→ Counter current contact of AL  
→ AL descends from the top of the columns and IBA ascends through the column by a pump.

→ Raffinate: Tar acids + IBA (higher quantity)  
Extract: AL + IBA (lower quantity)

### ② Extract and Raffinate Still Section

Objective: i) To separate solvent from tar acids  
ii) To recover entrained solvent from extract

done by distillation

# Steam stripping is the process for recovery of pure AL after distillation

→ Aq. NH<sub>3</sub> liq. of ~35%

Prof. BB, 4th Sep

## Catalyst deactivation

1) Coking

2) Sintering

3) Poisoning

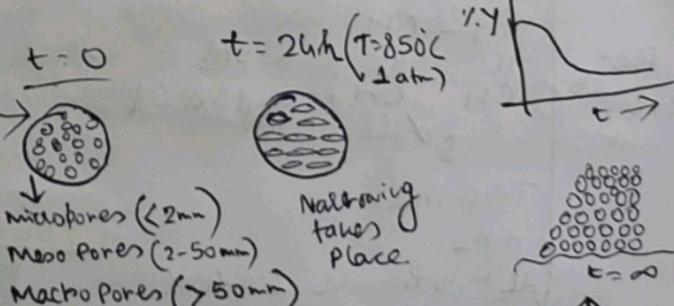
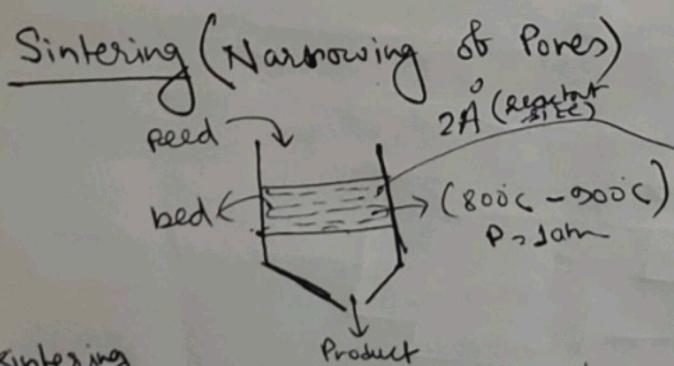
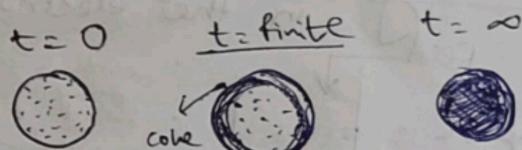
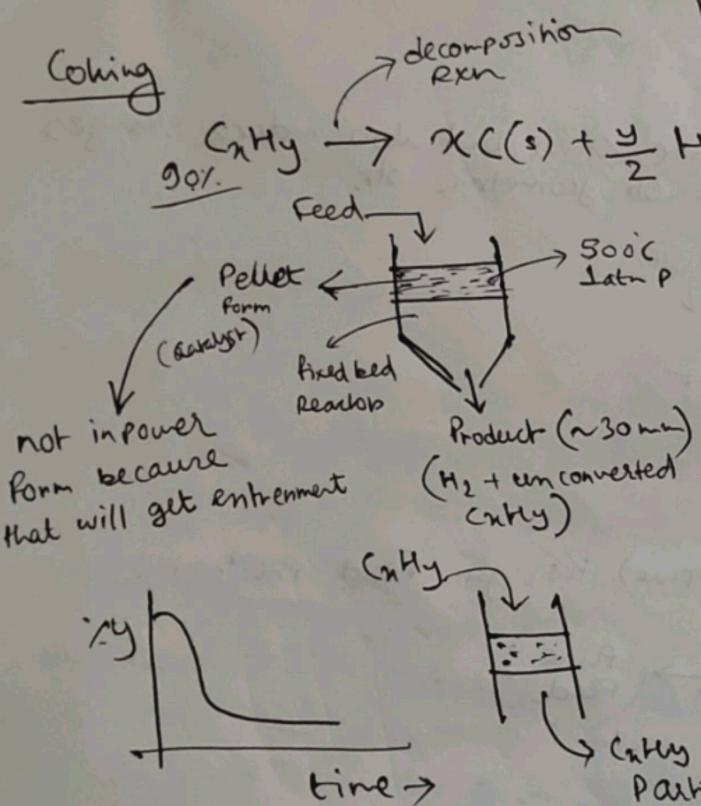
Narrowing of Pores

Aggregation of active metal/metal oxide particles.

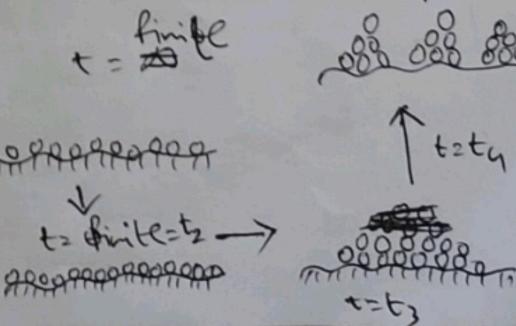
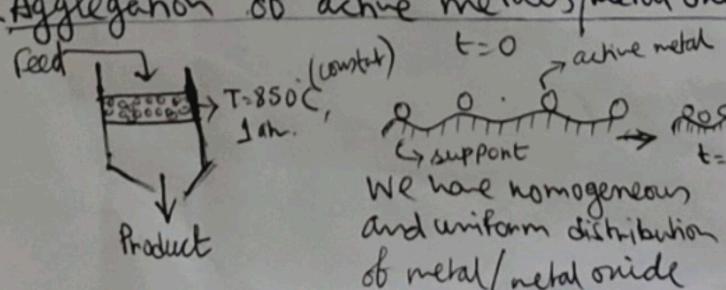
Coking: Com<sup>2+</sup> to reactions involving H-C-S.  
It results from a carbonaceous material (cane) deposited on the surface of a catalyst.  $\rightarrow$  (Pb, Hg, Zn, Sn, Cu, Fe)

Poisoning: Occurs when poisoning molecules are irreversibly chemisorbed to active sites, thereby reducing no. of sites for main reaction.

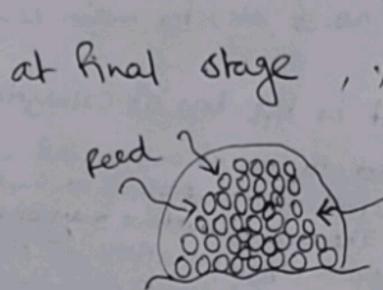
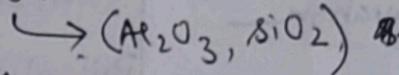
Sintering: It is the loss of catalytic activity due to loss of active surface area resulting from prolonged exposure to high gas phase temp. The active surface may be lost either by crystal agglomeration or closure of pores inside the catalyst pellet or narrowing of pores. A change in surface str. may also result.



## Sintering (Aggregation of active metals/metal oxide)



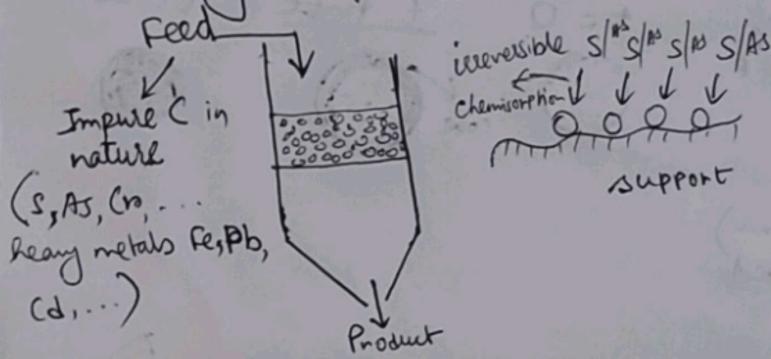
The distance b/w metal oxide are decreasing due to melting of oxide. The support is not melted as it is high thermal stability.



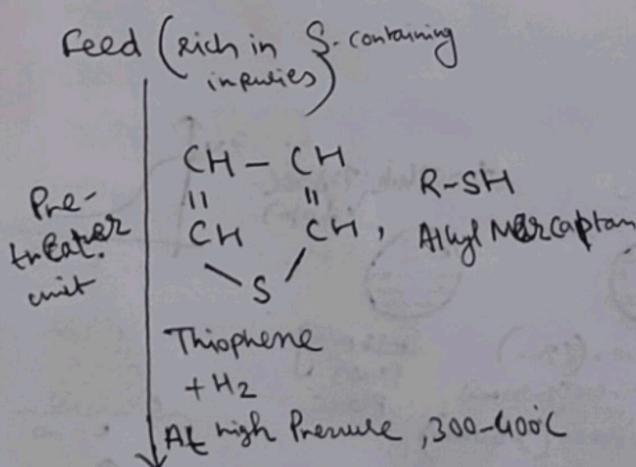
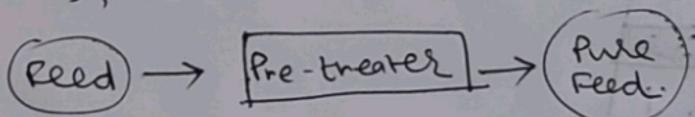
Productivity decrease because

the feed is not able to get in touch with the active internal metals, that part are not accessible.

# Poisoning: Not only block active sites, but also induce changes in the electronic or geometric str.



To avoid this, we can pass Reed (impure) through Feed Pre-treater



## Preparation of O<sub>2</sub>, N<sub>2</sub> from Air

### Air Separation Unit (A.S.U.)

#### Uses of O<sub>2</sub>

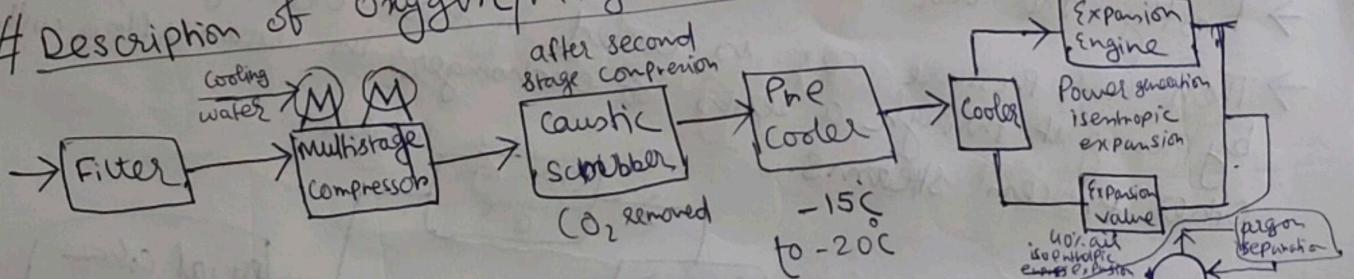
- i) Major use  $\rightarrow$  Production of steel in open-hearth furnace
- ii) Oxygen to remove scales by using oxyacetylene flame (steel industry)
- iii) In chemical industry  $\rightarrow$  e.g. acetylene and ethylene oxide production (large consumer, ~~not~~ Partial oxidation of hydrocarbons to produce NH<sub>3</sub>, CH<sub>3</sub>OH etc.)
- iv) Metal working, underground gasification, fire fighting, medical purpose etc.

#### Uses of N<sub>2</sub>

- i) Major usage of N<sub>2</sub> is in gaseous blanket (excluding oxygen/moisture)
- ii) To achieve extremely low temperature (-210°C)
- iii) To produce ammonia (NH<sub>3</sub>) industry as refrigerant and
- iv) Use in food processing transportation.

Boyle's  
cycle

### # Description of Oxygen/nitrogen plant

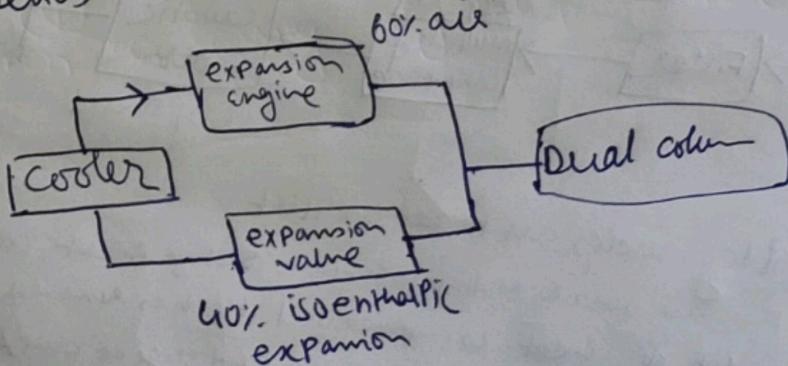


- Filter removes air to remove dirt
- Then air goes to multistage compressor, 5 stage present, compress the air, lot of heat is generated. Heat is removed by cooling water.
- Caustic Scrubber CO<sub>2</sub> is removed. [2nd stage of compression]
- 165-170 kg/cm<sup>2</sup> Pressure is attained after MS. compression [HP air]
- after final state of compression, air is taken to cooler to lower temp.

- After that, air successively goes through different stages -
- (i.e. N<sub>2</sub> cooler)
- Vaporisation cooler → Moisture ~~cooler~~<sup>separator</sup> → oil filter to remove all oil present → alumina dryer (remove left out moisture) → dust filter (remove suspended particles)
- (60% air)
- Expansion engine, expansion is done, some air got liquified
- rest 40% air goes to isenthalpic expansion

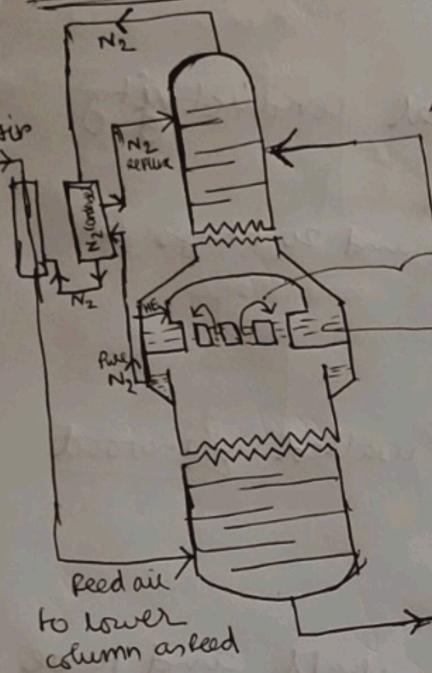
- Expansion valve give higher efficiency than expansion engine. Because expansion engine is used to generate the power to run the entire system.
- After that, send it to lower end of dual column.
- at middle of dual column
- Heat exchanger, condenser both lower column and reboiler for upper column.
- O<sub>2</sub> is heavy so comes at reboiler side

- Heylandt Cycle: is thermodynamic process used in A.S.U.S. for separation of air's primary component = N<sub>2</sub>, O<sub>2</sub>.
- For separation of air's primary component = N<sub>2</sub>, O<sub>2</sub>.
- For separation of air's primary component = N<sub>2</sub>, O<sub>2</sub>.
- firstly the air is compressed using a compressor.
- first the air is cooled in heat exchanger, typically by passing it through a series of exchangers in counterflow with other process streams.



11th Sep, S.S.

### Dual Column



Two tray type distillation column formed by a single heat exchanger at the middle.

# Heat exchanger:- Acts as condenser for the lower column, & reboiler for the upper

# Feed air after exchanging heat with waste ( $N_2$ ) the cold  $N_2$  product is fed to the feed tray of the lower column.

# 35% Pure  $O_2$  from the bottom of the lower tray, after exchanging heat in  $N_2$  superheater as fed to the upper column as feed. It is subcooled to avoid flashing in the column.

# The upper column pressure is  $0.5 \text{ kg/cm}^2$ , whereas lower column pressure is  $5 \text{ kg/cm}^2$ .

# Pure  $O_2$  is collected at the reboiler side of the upper column, the pure  $N_2$  is obtained at the condenser side of the lower column.

# The boiling point of  $O_2$  is  $12.8^\circ\text{C}$  more than that of  $N_2$ , so  $O_2$  descends through the column and  $N_2$  ascends.

#  $O_2$  Product is obtained as saturated vapour from the bottom of the upper column.

# All the streams which are introduced into the upper column at low pressure are subcooled in the  $N_2$  superheater to avoid throttling and flashing.

Throttling:- Process used to reduce pressure of a high pressure gas stream. It is ~~operated in the~~ employed to achieve the desired conditions in low-pressure column of a dual-column distillation system.

Flashing:- is a phase separation process used to separate high pressure gas liquid mixture into vapour and liq. phase. Commonly employed in high pressure column.

## MOC of dual column and trays:

Column → Brass column or cast iron with brass lining.

Trays → Brass/Cu for good thermal conductivity

For the production of  $400 \text{ m}^3/\text{hr. O}_2$ ,

no. of trays = 56 for upper column and 20 trays for lower column.

## Storage:

liq.  $\text{O}_2$  → specifically lagged double-walled glaswood insulated spherical shell.

gaseous  $\text{O}_2$  → Cu-shell holders.

# Heat exchanger and cooler are shell and tube type. Brass tube with mild steel shell.

## # Importance of <sup>Coke</sup> Coal in steel Industry —

i) Coke as fuel: it is used to produce the heat needed to melt the iron ore and limestone.

ii) Coke is a Reducing Agent: It ~~takes the~~ takes the oxygen out of iron ore, leaving only the pure iron.

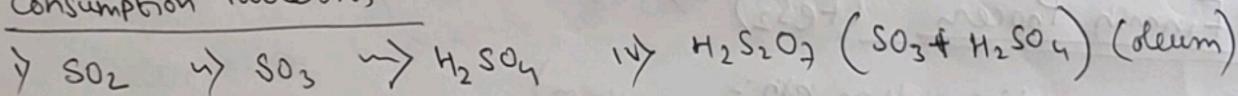
Prof. B.B | 11th Sep

## S and $H_2SO_4$ Manufacturing

### Properties

- i) At. weight 32.07
- ii) Allotropes
  - Rhomboic (112.8°C)
  - Monoclinic sulphur (119°C)
- iii) B.P = 444.6°C
- iv) Solubility = Insoluble in water, soluble in liq.  $NH_3$  ( $NH_4OH$ ) and organic solvents.
- v) Availability →
  - Powder
  - Molten state
  - Rock → Lumps.

### Consumption Patterns



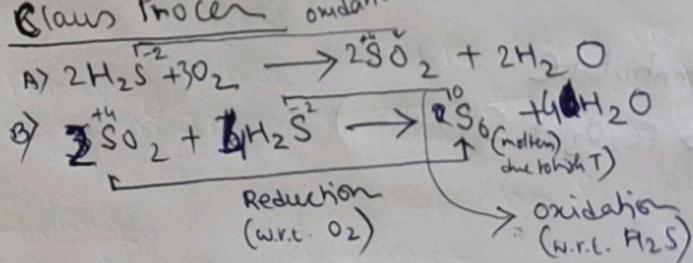
### End Application

- Gunpowder ( $C + S + KNO_3$ )
- Inorganic chemical manufacturing industries.
- Organic chemical
- Paint Industry, Polymer industry, Rubber Industry, Paper-RuP industry

### Production of Elemental Sulphur

- i) Frasch Process (USA)
- ii) Claus Process (USA + India)
  - Oxidation and reduction of  $H_2S$
- iii) Finnish Process (India)
  - (40-45% S)

### Claus Process



### Coking

↓ (carbon layer) → ↓ (catalytic Activity)

Possibility 1 [less metal-support interaction]

active metals → carbon nanotubes [Tip Growth]  
support

Possibility 2 [More metal-Support interaction]

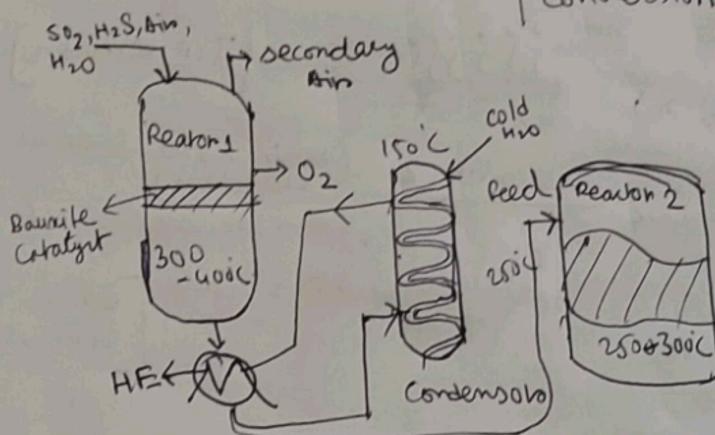
tips are unoccupied

support → active metals [Bare Growth]

### Reactor I

T = 300-400°C  
P = 1 atm

Catalyst = Bauxite ( $\text{Al}_2\text{O}_3$ )  
Conversion = 70-80%



### Reaction - II

T = 250°C - 300°C  
P = 1 atm

Catalyst =  $\text{Al}_2\text{O}_3$   
Conversion = 95-99%

⇒ Reason of 2 reactions

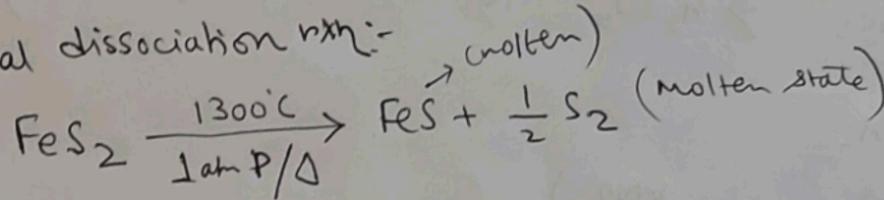
Main aim is to get more yield of sulphur. In II-nd reactor we get 99% conversion. But if we use only that

then hotspot formation will take place and conversion will be less. So to avoid hotspot formation ...

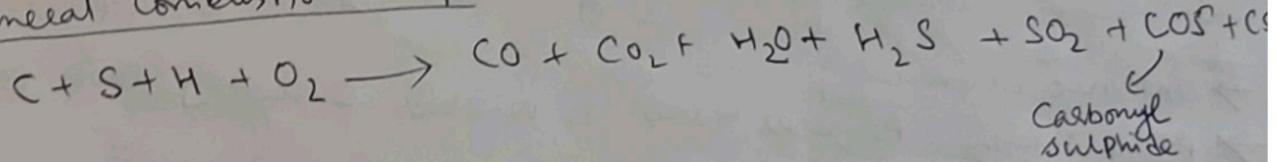
upon pyrites.

### Finnish Process ( $\text{FeS}_2$ ) → 40-45% S

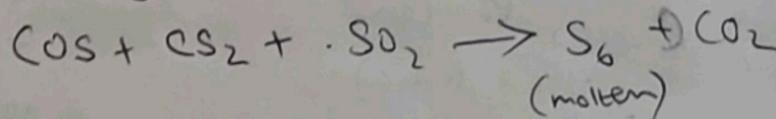
Thermal dissociation rxn:-



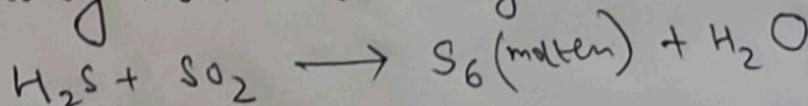
General Combustion Rxn



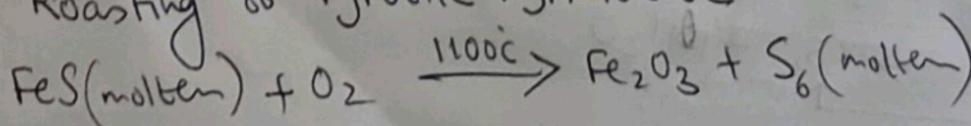
S-Recovery from Hot stage (600°C, 1 atm,  $\text{Al}_2\text{O}_3$  catalyst)



S-Recovery from cold storage



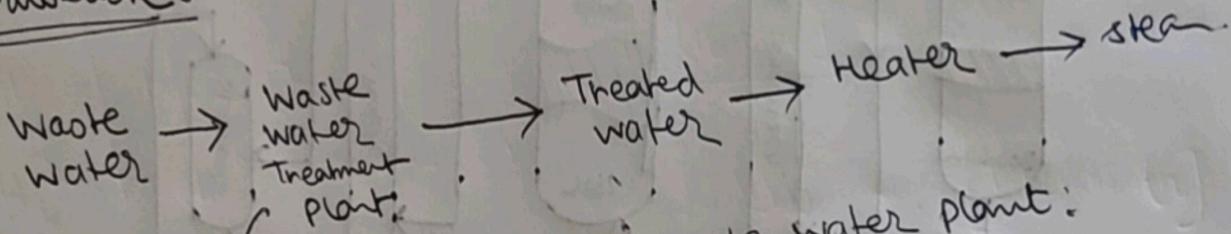
Roasting of Pyrotite Pyrrhotite



## ① Frasch Process (USA) [high purity of S]

Steaming salt domes + steam → elemental sulphur  
Corrodes surface of reactor

Drawback: Sulfur formed



operations carried out in a waste water plant:

a) Chlorination (+ Cl<sub>2</sub>) → treated water / fresh water

b) Ozonation (+ O<sub>3</sub>) → fresh water

c) Advanced oxidation process (+ O<sub>2</sub>, at P ↑, T = 250°C, 10 bar)

d) Fenton Rxn (FeSO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub>)

→ major engineering problems:—

i) Corrosion of surface of reactor by elemental S.

ii)

→ Scrubbing operation —

S contain acidic impurities. Scrubbing with mono ethanol amine  
Produces S (free of impurities)

