fuel

Fuel → Fuel is a combustible substance, which contains carbon as a main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and industrial purpose.

Fossil fuel → is a general term for buried combustible geologic deposits of organic materials formed from decayed plants and animals that have been converted to crude oil, coal, Natural gas.

Nuclear fuel → It is fuel that is used in a Nuclear reactor to sustain a Nuclear chain reaction

Combustion

$$C_xH_y + \frac{z}{2}O_2 \longrightarrow x\,CO_2 + \frac{y}{2}H_2O + \Delta$$

WR

Classification of fuel

Chemical fuel

↓

On the basis of occurrence

- Primary / Natural fuels
  - Raw coal
  - Solid fuel → Wood, Coal
  - Liquid fuel → Crude oil
  - gaseous fuel → Natural gas
- Secondary / Derived fuel
  - Petrol Made
    - On the basis of State
      - Solid → Coke, Charcoal
      - liquid → Petrol, Diesel
      - Gaseous → Coal gas, Biogas

Composition of Producer gas → $CO + N_2$

Steam / water gas → $CO + H_2$

Characteristics of good fuel

reason

1) High calorific value
2) Moderate Ignition temperature (हम इसको good criteria में क्यों लेते हैं)
3) Low content of non-combustile Matter
4) Low Moisture content
5) Easy to transport
6) Easy Storage
7) It should be efficient
8) Economical
9) CP (Combustion product) like ash residue left after combustion so we require low C.P.

Calorific value

Calorific value is the amount of heat liberated by the complete combustion of a unit Mass of a fuel.
The quantity of heat can be Measure by the following units

a) Calorie
b) Kilocalorie
c) British thermal units
d) Centigrade heat units

Unit of calorific value

cal / gram
kilocal / Kg

1 Kcal = 1000 cal

Kcal / Kg

cal / Cc

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Comparative Study of Solid, liquid, gaseous fuel

Fuel characteristics	Solid	liquid	gas
① Calorific value	least	Higher	Highest
② Combustion rate	slow	Quick	very rapid
③ Combustion control	Not easy	Controllable	Controllable
④ Smoke	Invariably produced (yes)	less	No Smoke
⑤ Ash	yes	No	No
⑥ Risk of fire hazards	least	greater	very High
⑦ Cost	cheapest	Moderate	expensive
⑧ Storage	easy	Not easy	Not easy
⑨ Transportation Cost	High	Low	low

GCV > NCV

Higher or Gross Calorific value (HCV / GCV)
It is the total amount of heat liberated when unit mass or unit volume of the fuel has been burnt completely and the product of combustion are cooled to room temperature.

- Total amount of heat
- GCV → Latent heat of vaporization

High calorific value (Latent heat of water included)
Lower or Net Calorific value (LCV / NCV)
It is the net heat produced when unit mass or unit volume of the fuel is burnt completely and the combustion product are allowed to escape.

- Total heat taken out by combustion product.
- Lower Calorific value (Latent heat Substracted from gross)

$$NCV = GCV - 9 \times \text{wt of hydrogen} \times 587 \text{ cal/g}$$

when wt of hydrogen = 0
when No hydrogen in fuel

$$NCV = GCV - 9 \times 0 \times 587$$
$$NCV = GCV$$

British Thermal Unit (B.Th.U or BTU) It is the quantity of heat required to increase the temperature of 1 pound of water through 1° Farenheit

1 BTh U = 252 cal = 0.252 kcal
1 kcal = 3.968 BTh U = 2.2 CHU

Date

Q) Solid fuel has calorific value 9000 cal/g Express in British Thermal unit.

Sol)

1 BTU = 252 calories

$\frac{1}{252}$ BTU = 1 calories

$\frac{9000}{252}$ BTU = 9000 calories

$\boxed{\frac{9000}{252} \text{ BTU}}$ Ans

Bomb Calorimeter

Determination of calorific value of solid fuel / non volatile fuel by Bom calorimeter

Calorimeter → It is a device which is used to calculate the calorific value.

Bomb calorimeter →

A Bomb calorimeter is a Constant - volume Calorimeter, constructed to withstand the pressure produced by the reaction as it heats the air within the container. The temperature change of water is used to calculate the heat of combustion

Principle

Total Heat released = Total heat absorbed during combustion

This apparatus is used to calculate the calorific value of Solid and non - volatile liquid fuel

A known mass of fuel is burnt in excess of oxygen and Heat liberated is transferred to known amount of water.

Date

Construction

1) Stainless steel cylindrical Bomb (pressure inside it is 50 atm) containing.
   - Air tight sealed lid
   - Oxygen inlet
   - 2 stainless steel electrode connected to an external battery.
   - Small ring attached to one electrode which act as support for crucible
   - Crucible containing fuel placed on the Small ring Magnesium pt wire.
2) Copper Calorimeter → Steel bomb is placed in Copper Calorimeter containing
   - known Amount of water
   - Beckmann thermometer
   - Mechanical stirrer
3) Air jacket
4) Water jacket

Copper Calorimeter is surrounded by this air jacket and water jacket to prevent any loss of heat due to radiation

Working

A known amount of fuel (0.5 to 1g) is taken in the crucible supported over the ring.
Stretch the fuse wire (fine Mg wire) over electrode touching the fuel Sample.

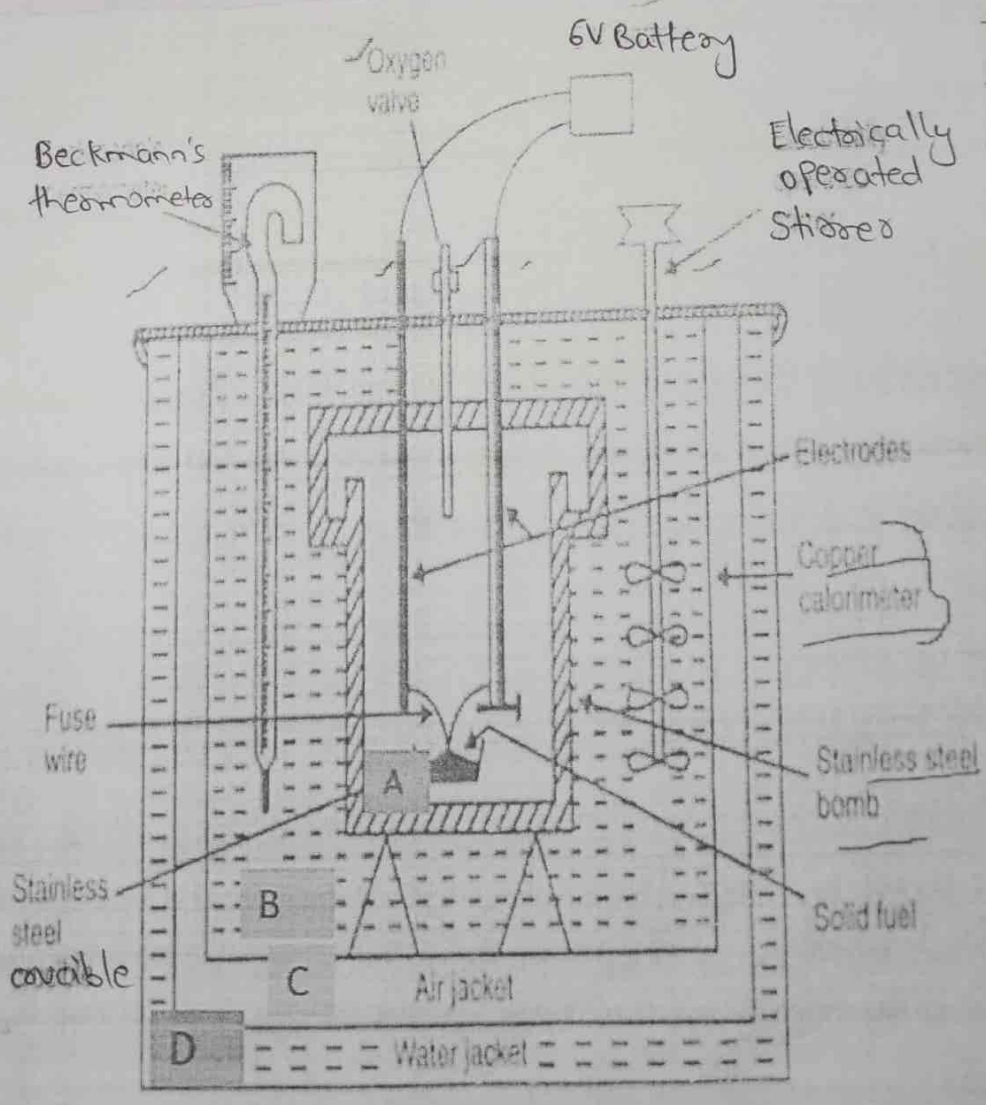
Tightly screwed the bomb lid

fill the bomb with oxygen to 25 - 30 atmosphere

pressure
place the bomb in copper calorimeter containing a known amount of water after stirring note initial temperature of water with the help of Beckmann thermometer.

Connect the electrode with 6 volt battery and complete the circuit.

Combustion of fuel with release of heat
Transfer of heat to water present in calorimeter
Note the final temperature reading.



Bomb Calorimeter

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Observation

Let Amount of fuel taken in crucible = x gram
" " " water taken in calorimeter = W gram
" " " water equivalent = w gram
" " calorific value of fuel = C cal/gram
Heat released = $x\ C$ calories

Initial Temperature = $T_1°C$
final Temperature = $T_2°C$

Heat absorbed by water = $W \times S \times (T_2 - T_1)$

$$S = \frac{Q}{m \times \Delta T}$$

Heat absorbed by water = $W \times S \times (T_2 - T_1)$
Heat absorbed by water equivalent = $w \times S \times (T_2 - T_1)$

Sp of water = 1 cal/g °C

Total heat absorb = $W S (T_2 - T_1) + w S (T_2 - T_1)$

$$= (W + w)(T_2 - T_1) S$$

$$= (W + w)(T_2 - T_1)$$

$$x\ C = (W + w)(T_2 - T_1)$$

$$GCV = C = \frac{(W + w)(T_2 - T_1)}{x}$$

$$NCV = GCV - 9 \times \text{wt of } H \times 587 \text{ cal/gm}$$

Date

Correction in Bomb calorimeter

a) Fuse wire correction → Heat released due to ignition of fuse wire should be substracted.

b) Acid Correction → Fuel containing S and N oxidize to H_2SO_4 & HNO_3 under high temperature and pressure of ignition

$$S + 2H + 2O_2 \longrightarrow H_2SO_4 + \text{Heat}$$

The amount of these acid correction analyzed by washing of the Calorimeter

for each ml of $\frac{N}{10}$ H_2SO_4 formed 3.6 cal this should be substracted.

1 mg of S = 2.52 Cal this should be substracted

1 ml of $\frac{N}{10}$ HNO_3 = 1.43 cal this should be substracted

c) Cooling correction

$$\text{GCV of fuel (C)} = \frac{(W+w)(T_2 - T_1 + \text{cooling correction}) - (\text{Acid} + \text{fuse correction})}{\text{Mass of fuels}}$$

Date

Q) In a Bomb calorimeter experiment the following data were obtained
wt of coal = 0.83g
wt of water taken in calorimeter = 1365g
wt of water equivalent of calorimeter = 135g
initial T = 26.5°C
final T = 29.2°C
calculate the GCV & NCV of fuel if it contains 8% of Hydrogen

Sol)

$$GCV = \frac{(W+w)(T_2 - T_1)}{x} \qquad x = 0.83$$

$$= \frac{(1365 + 135) \times (29.2 - 26.5)}{0.83}$$

$$= 4879.51 \text{ cal/g}$$

$$NCV = GCV - 9 \times H \times 587$$

$$= 4879.51 - 9 \times \frac{8}{100} \times 587$$

$$= 4456.87 \text{ cal/g}$$

Q) A sample of coal contain C = 94% H = 5% ash = 1% The following data were obtained when the above coal was tested in bomb Calorimeter.
wt of coal = 0.95g
wt of water taken = 700g
wt of water equivalent of calorimeter = 2000g
Increase in Temperature = 2.48°C
Use wire correction = 10.0 cal

acid correction = 60.0 cal

Cooling Correcting = 0.02 °C

calculate GCV & NCV (Latent heat of Condensation of steam = 587 cal/g).

Sol) Wt of coal (x) = 0.95 g

W = 700

w = 2000

$t_1 - t_2$ = 2.48°C

fuse wire correction = 10.0 cal

acid correction = 60.0 cal

Cooling correction = 0.02° C

$$GCV = \frac{(W+w)(T_2 - T_1 + \text{cooling correction}) - (\text{acid} + \text{fuse wire correction})}{\text{Mass of fuel}}$$

$$GCV = \frac{(700+2000)(2.48+0.02) - (60+10)}{0.95}$$

$$= 7031.57 \text{ cal/g}$$

$$NCV = GCV - 9 \times H \times 587$$

$$= 7031.57 - 9 \times \frac{5}{100} \times 587$$

$$= 6767.42 \text{ cal/gm}$$

Note

In a bomb calorimeter does the reaction takes place under conditions of

a) Constant pressure X

b) Constant volume ✓

Bay's gas calorimeter

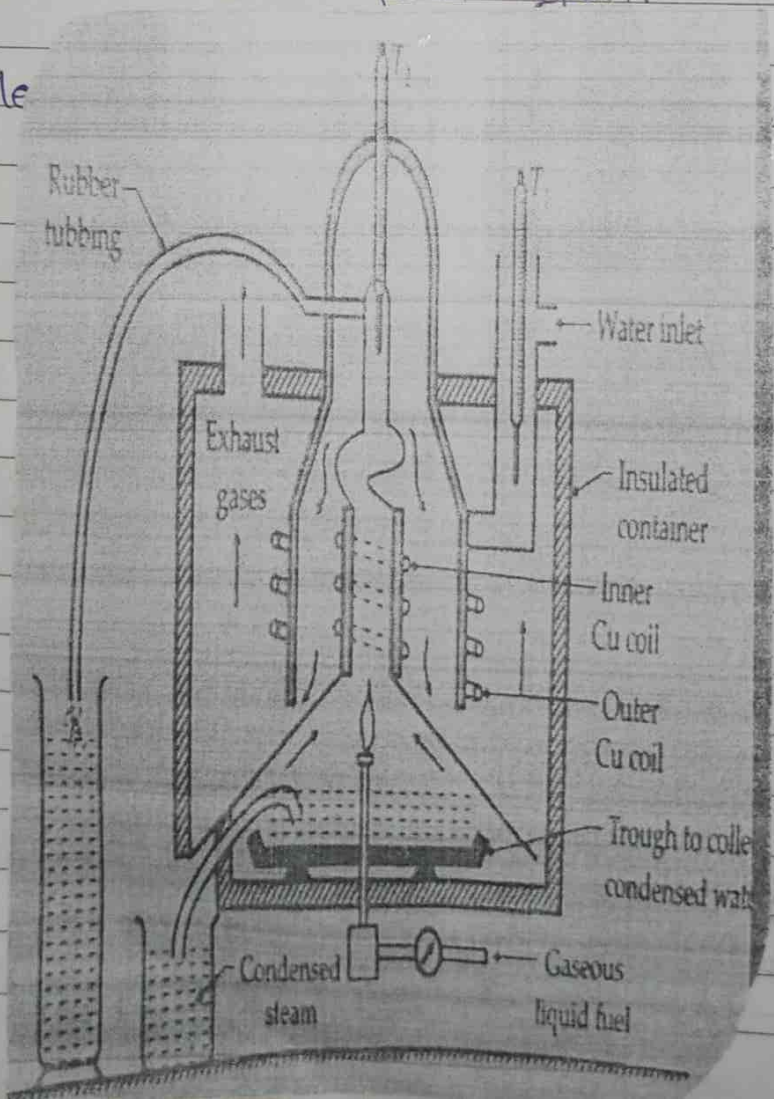
It is used for determination of calorific value of gaseous and volatile liquid fuel.

Principle

The gaseous fuel is burned in a vessel at a constant rate in such a manner that the entire heat is absorbed by water which is circulated in a chimney around the burner. From the volume of the gaseous fuel burnt the volume of water collected and the rise of temperature of water and the calorific value of fuel is determined.

Heat lost = heat gain.

He ...bed



Construction

1) Gas burner → It consist of suitable gas burner in which a known volume of gas at a known pressure is burnt at a uniform rate.
2) Combustion chamber or chimney
Round the burner there is a chimney or combustion chamber having copper tubing coiled inside as well as outside it. Water at a constant rate enters at the top of the outer coil passes through the outer coil. Moves to the bottom of the chimney and then moves upward through the inner coil and exit from the top.
3) Thermometer
The thermometer T1 & T2 are fitted to note the temperature of the incoming and outgoing water respectively.
4) Container
A container is provided to collect water formed due to condensation of steam produced during combustion
5) Insulated chamber
The whole assembly is enclosed in an insulated chamber.

Burning of fuel and circulation of water are continued for about 15 minutes for initial warming up period.
When the Calorimeter get warmed the rates of fuel burning and water circulation are adjusted so that exit water leaves the apparatus nearly at atmospheric pressure

Heat produced by burning of gaseous fuel is transferred to water in the copper coil and the steam formed inside the chimney during combustion gets condensed to water which is collected in the provided container Reading are noted when conditions become steady.

observation

let volume of gaseous fuel burnt at STP = V m^3
Initial Temperature t_1 °C
final Temperature t_2 °C
wt of water collected = W kg
wt of water condensed = m kg

calorific value of fuel = C kcal/m^3

Heat released = VC kcal
Heat absorbed = $W \times S \times (t_2 - t_1)$

$VC = W S (t_2 - t_1)$

$VC = w(t_2 - t_1)$

$$GCV = C = \frac{W(t_2 - t_1)}{V}$$

V m^3 of gas = m kg of water
1 m^3 of gas = $\frac{m}{V}$ kg of water

Latent heat of vaporization = $\frac{m}{V} \times 587$ kcal/m^3

NCV = GCV - Latent heat of vaporization

$$NCV = GCV - \frac{m}{V} \times 587 \quad K\,cal/m^3$$

(2) During the determination of calorific value of a gaseous fuel by Boy's calorimeter the following result were noted.
volume of gaseous fuel burnt at NTP = 0.098 m^3
wt of water heated = 50 kg
wt of steam condensed = 0.051 kg
Temperature of incoming water = 26.1°C
Temperature of outgoing water = 46.5°C
Determine the GCV & NCV of fuel

Sol)

$$GCV = \frac{W(t_2 - t_1)}{V} \quad K\,cal/m^3$$

$$= \frac{50(46.5 - 26.1)}{0.098}$$

$$= 10408.2 \; K\,cal/m^3$$

$$NCV = GCV - \frac{m \times 587}{V}$$

$$= 10408.2 - \frac{0.051 \times 587}{0.098}$$

$$= 10102.7 \quad K\,cal/m^3$$

Dulong's formula

Carbon
Hydrogen
Oxygen
Sulphur

$$GCV = \frac{1}{100}\left[8080\,(\%C) + 34500\left(\%H - \frac{\%O}{8}\right) + 2240\,(\%S)\right] \text{ cal/gm}$$

$$NCV = GCV - 9\,H \times 587 \text{ cal/gm}$$

Q) Calculate the gross & Net Calorific value of the following Composition

C% = 80%
O = 5%
N = 1.4%
H = 9%
Ash = 2.1%
S = 2.5%

Sol)

$$GCV = \frac{1}{100}\left[8080 \times 80 + 34500\left(9 - \frac{5}{8}\right) + 2270 \times 2.5\right]$$

$$= 8828.025 \text{ K cal/kg}$$

$$NCV = 8828.05 - 9 \times 587 \times \frac{9}{100}$$

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NM

Q) Calculate GCV & NCV using Dulong's formula

	C	O	S	N	Ash	H
i)	80%	5%	2.5%	1.4%	2.1%	rest

Sol)

Concept

$$C + O + S + N + Ash + H = 100$$

$$H = 100 - C - O - S - N - Ash$$

$$H = 100 - 80 - 5 - 2.5 - 1.4 - 2.1$$

$$\boxed{H = 9\%}$$

use Dulong formula for Numerical

Classification of coal according to ranks

Type of Coal	Percentage of Carbon	Calorific Value
Wood	40 - 45	3500 - 4500
Peat	45 - 60	4125 - 5200
~~Brown~~ Lignite (Brown coal)	60 - 75	6600 - 7100
Bituminous coal	75 - 90	6600 - 8800
Anthracite	> 90%	> 8400

Date

W2

Analysis of coal

Proximate analysis

1. Data varies with the procedure adopted and hence it is called Proximate analysis
2. It gives information about the quality of coal
3. It determine moisture content, volatile matter, ash & fixed carbon content

Ultimate analysis

A) Proximate Analysis (Type)

1) Moisture content

1 to 2g of Powdered coal Sample (W) $\xrightarrow[1 \text{ hours}]{105^\circ C - 110^\circ C}$ cooled down to Room temp (W_1)

$$\% \text{ Moisture content} = \frac{\text{Loss of wt of coal sample}}{\text{Initial wt of coal sample}}$$

$$= \left(\frac{W - W_1}{W}\right) \times 100$$

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(2) Volatile Matter (Higher % is undesirable)

Moisture free sample (1g of carbon) $\xrightarrow[7\ min]{950 \pm 20^\circ C}$ Cooled down & stare (W_2) weight

$$\% \text{ of volatile Matter} = \frac{\text{Loss of wt of sample}}{\text{initial wt of coal}} = \left(\frac{W_2 - W_1}{W}\right) \times 100$$

(3) Ash content / Non combustible Content

Moisture Content & volatile Matter free Sample $\xrightarrow[1/2\ hr]{750 \pm 20^\circ C}$ wt of residue (W_3)

$$\% \text{ Ash content} = \frac{\text{wt of residue}}{\text{initial weight of coal}} \times 100 = \frac{W_3}{W} \times 100$$

(4) fixed carbon

$$\text{fixed C} = 100 - [\% \text{ Moisture content} + \% \text{ of volatile Matter} + \% \text{ of Ash content}]$$

% fixed Carbon ↑ = Good Quality coal ↑

Significance of Proximate analysis

(1) % fixed carbon ↑ Higher then greater Calorific value
(2) Fixed carbon acts as a main heat generator during burning
(3) High volatile Matter content indicates easy ignition of fuel.

Numerical

Boximate analysis

Q1) 2.0 gm of coal sample was heated in a Silica crucible for 1 hour at 110°C The residue was cooled down to room temp & its weight was 1.975 gram. Then it is covered with a ~~vented~~ vented lid & strongly heated for exactly 7 mins at 950 ± 20°C The residue weight was 1.328 gm. Then the residue was heated without cover till a constant weight was obtained. The residue weight was 0.204 gm. Calculate the % of Moisture content, volatile Matter, Ash content & fixed C.

Sol) Initial wt of coal sample (W) = 2 gm

wt of coal sample after heating (W_1) at 110°C = 1.975 gm

wt of coal sample after heating at (W_2) 950 ± 20°C = 1.328 gm

wt of residue of left (W_3) = 0.204 gm

% Moisture content = ~~2-0~~.

$$\frac{2 - 1.975}{2} \times 100$$

% Volatile Matter = $\frac{1.975 - 1.328}{2} \times 100$

% ash content = $\frac{0.209}{2} \times 100$

% Fixed C = $100 - [\%.MC + \%.VM + \%.Ash\ content]$

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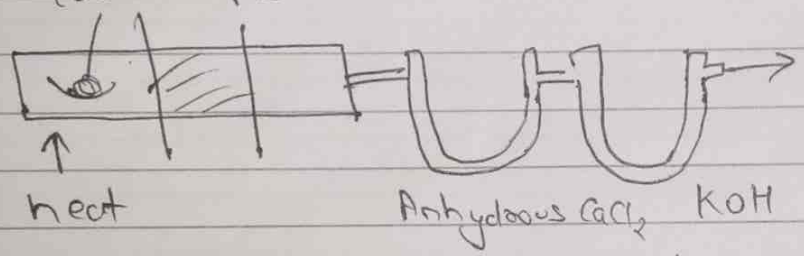
Ultimate analysis (Elemental analysis)

It is useful for combustion calculation.
Ultimate analysis also known as elemental analysis it is method used to determine the carbon, Hydrogen, Nitrogen, Sulphur and oxygen content present in Solid fuel.

Ultimate analysis (C, H, N, O, S)

① % of C & H — combustion gives both carbon, water and heat during combustion of coal



More % of C & H More good coal fuel

$x \rightarrow w_1 g$ $\quad W \rightarrow w_2 g$

$C \rightarrow CO_2 + KOH \rightarrow K_2CO_3 + H_2O$

$H_2 \rightarrow H_2O \rightarrow$ Anhydrous $CaCl_2 \rightarrow CaCl_2 . 7H_2O$

$C + O_2 \rightarrow CO_2$
$12g \quad 44g$

$$\% \text{ of } C = \frac{12}{44} \times \frac{\text{Increased wt of KOH tube due to absorption of } CO_2}{\text{Initial wt of coal taken}} \times 100$$

$$\% \text{ of } H = \frac{2}{18} \times \frac{\text{Increased wt of } CaCl_2 \text{ tube due to absorption of } H_2O}{\text{Initial wt of coal taken}} \times 100$$

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(2) Determination of N

$$\% \text{ of } N = \frac{1.4 \; N_1 V_1}{\text{wt of coal Sample}}$$

V_1 = volume of used acid for Neutralization

N_1 = Normality of acid

NZ

Q1) 1.56 g of coal Sample was kjobl halized and NH_3 gas this released, was absorbed in 50 ml of 0.1 N H_2SO_4 After absorption the excess acid required 6.25 ml of 0.1 N of NaOH for exact Neutralization, calculate the % of N.

Sol)

$$\% \text{ of } N = \frac{1.4 \times N_1 V_1}{\text{wt of coal Sample}}$$

$\Rightarrow$ wt of coal sample = 1.56 g

$\Rightarrow$ Volume of acid used for neutralization of NH_3 = (50 - 6.25) ml = 43.75 ml

Normality of acid = 0.1 N

$$\% \text{ of } N = \frac{1.4 \times 43.75 \times 0.1}{1.56}$$

(3) % of S

$$S + O_2 \longrightarrow SO_2 \xrightarrow{H_2O_2} H_2SO_4 + BaCl_2 \longrightarrow BaSO_4$$

$$\% \text{ of } S = \frac{32}{233} \times \frac{\text{wt of } BaSO_4 \text{ ppt}}{\text{Initial wt of coal Sample}} \times 100$$

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2g of coal sample in a quantitative analysis gives 0.175gm of $BaSO_4$. Calculate % of S

Sol)

$$\% S = \frac{32}{233} \times \frac{0.175}{2} \times 100$$

(4) % of ash

$$\frac{\text{weight of ash left}}{\text{weight of coal taken}} \times 100$$

(5) % of Oxygen (O)

$$\% \text{ of } O = 100 - \%[C + H + N + S + Ash]$$

(6) 1g of sample of coal was used in a bomb calorimeter for the determination of calorific value. Calorific value of coal was found to be 8800 cal/g The ash formed in the bomb calorimeter was extracted with acid and the acid extract was heated with barium nitrate solution and a precipitate of Barium sulphate was obtained The precipitate was filtered, dried and weigh The weight of precipitate was found to be 0.08g Calculate the % of sulphur in the coal sample.

Sol)

$$\% \text{ of } S = \frac{\text{wt of } BaSO_4 \text{ ppt obtained} \times 32 \times 100}{233 \times \text{wt of coal sample taken}}$$

$$\Rightarrow \frac{0.08 \times 32 \times 100}{233 \times 1} = 1.098\%$$

Carbonization Process (Destructive distillation)

The process of converting coal into coke is called carbonization

$$\text{Coal} \xrightarrow[\text{in absence of air}]{\text{High Temp}} \text{coke}$$

The decomposition of coal by heating it in the absence of air to give a solid residue, coke is called carbonization.

% of coal ↓

Soft

Not important

Coal

↓ 100°C

Moisture Content ⟶

↓

H_2S, SO_2 ⟶

↓ 350°C

Softening of coal

↓

tarry vapours

C% ↑

Hard

i.e. Hard, ~~lustrous~~

Calorific value

Strong, lustrous & coherent mass

600 - 700°C → H_2 gas ≥700°C → organic compound decomposition

↓

Strong Coke

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Answer

(1) Coal does not posses as much strength and porosity as coke
(2) Coke burns with short flame, ~~coke~~ Coal burn with a long flame
(3) By coking, undesirable sulphur is removed
(4) We coke but not coal is used as fuel for Metallurgical Processes

We

Coal	Coke
1) Calorific value is less	1) Calorific value is high
2) Mechanical strength of coal is less	2) Mechanical strength of coke is higher
3) Coal is formed by decaying Materials by the action of heat and pressure	3) Coke is formed by heating of coal in absence of air

Type of carbonization

1) Low temp carbonization
i) Coal is heated 500 - 700°C
ii) The yield of coke is about 75 - 80%
iii) ~~Vo~~ volatile Matter (5 - 15%)
iv) Mechanical strength → low
v) Nature → Soft
vi) use → Domestic purpose
vii) By products gas produced has a Calorific value of 6500 - 9500 kcal/m³

3) High temperature carbonization
i) High temp (900 - 1200°C)
ii) yield of coke (65 - 75%) ~~Carbon~~
iii) Volatile Matter (1 - 3%)
iv) Nature → Hard
v) Use → Industrial

vi) Mechanical Strength → High

vii) By product gas produced has a calorific value of about 5400 - 6000 Kcal/m^3

VI Manufacture of coke

Otto - Hoffman oven ✂ By product oven process

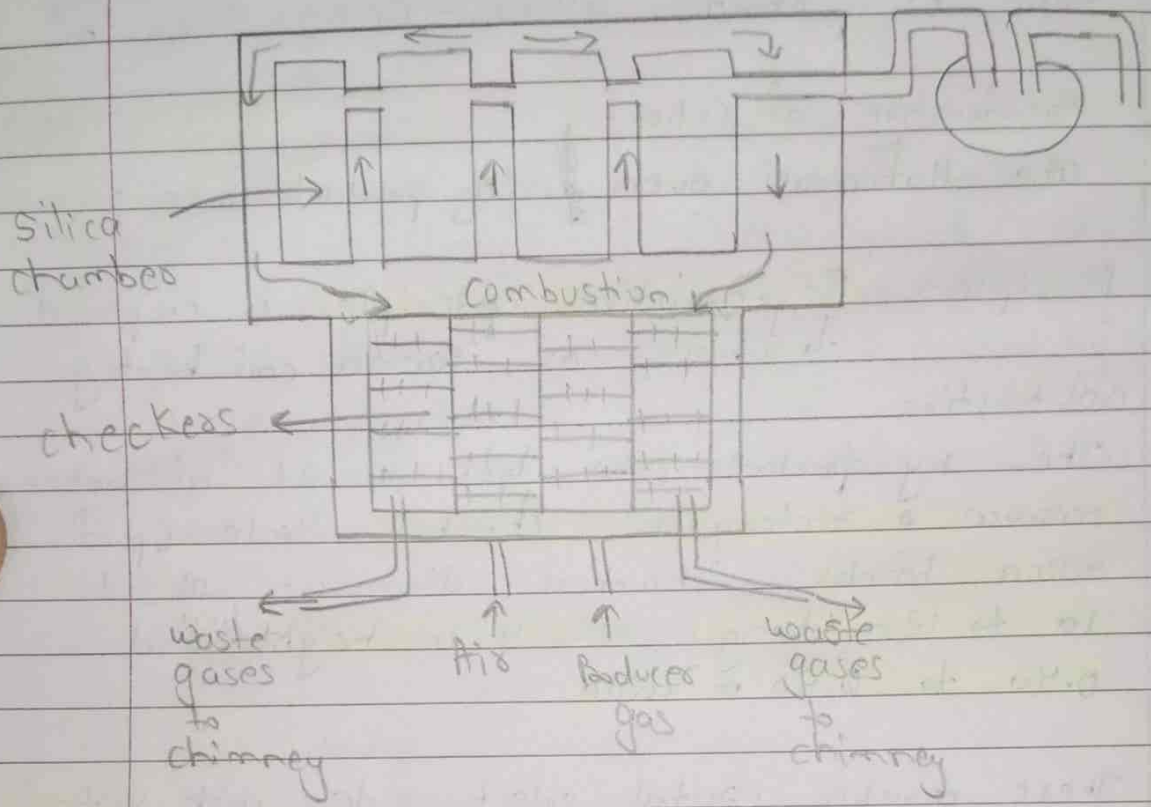
Principle → Regenerative principle is employed to achieve as economical heating

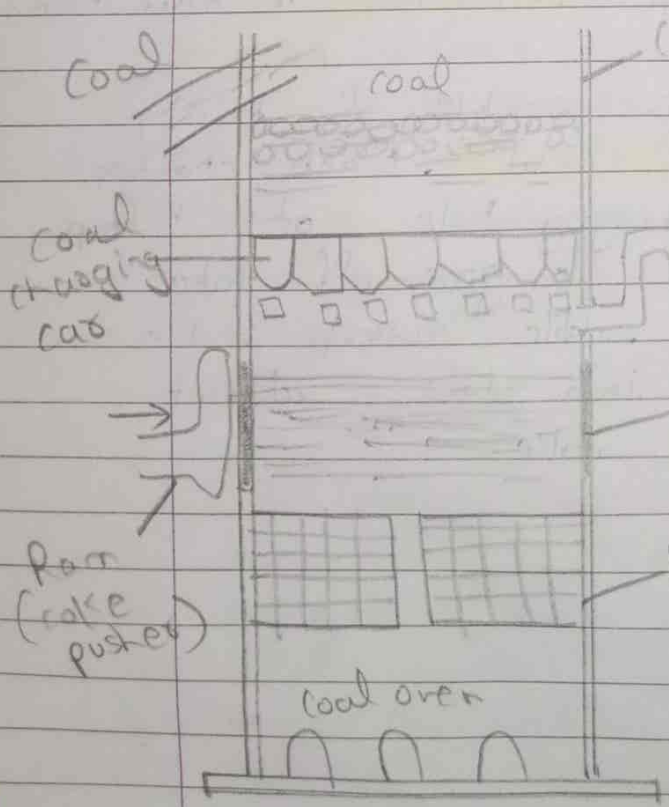
Construction

The by product coke oven consist of number of narrow rectangular chamber made up of silica bricks, chambers dimension about 10 to 12 m long, 3 to 4 m height and 0.40 to 0.50 m wide.

These chambers erected side by side with vertical flues or interspace for combustion in b/w them.

One single chamber is capable of holding 16 to 24 tonnes of coal. Each chamber is provided with a charging hole at the top (for charging coal) a gas off-take (for the removal of volatile matter) and a refractory-lined cast iron door at each ends for discharging coke.


silica chamber
Combustion
checkers
waste gases to chimney
Air
Producer gas
waste gases to chimney


Coal
coal
coal bunker
coal gas
coal charging car
coke chamber
Ram (coke pusher)
Regenerators
coal oven

Working

Coal is enter with the help of coal charging door then it with the help of coal car it enters into the coal bunker then the chamber are closed tightly at both end to prevent any access of air. Then the producer gas are produced in it at the bottom of the container and the temperature is 1200°C then due to the high temperature the coal burns and combustion takes places. Due to the combustion some amount of gases are waste which has been trap from the waste gases to chimney. In this the waste gases are coming they again heat the checkers through which the waste gas is in our use and the thermal efficiency, fuel efficiency increases. The hot coke is taken and the Quenching process takes places. (Quenching process → rapid cooling or Make the Material temperature room temperature).

Quenching are done by two ways

a) Wet Quenching → hot coke पर water डाला जाता है

b) Dry Quenching → hot coke को inert gas की सहायता से cool करा जाता है

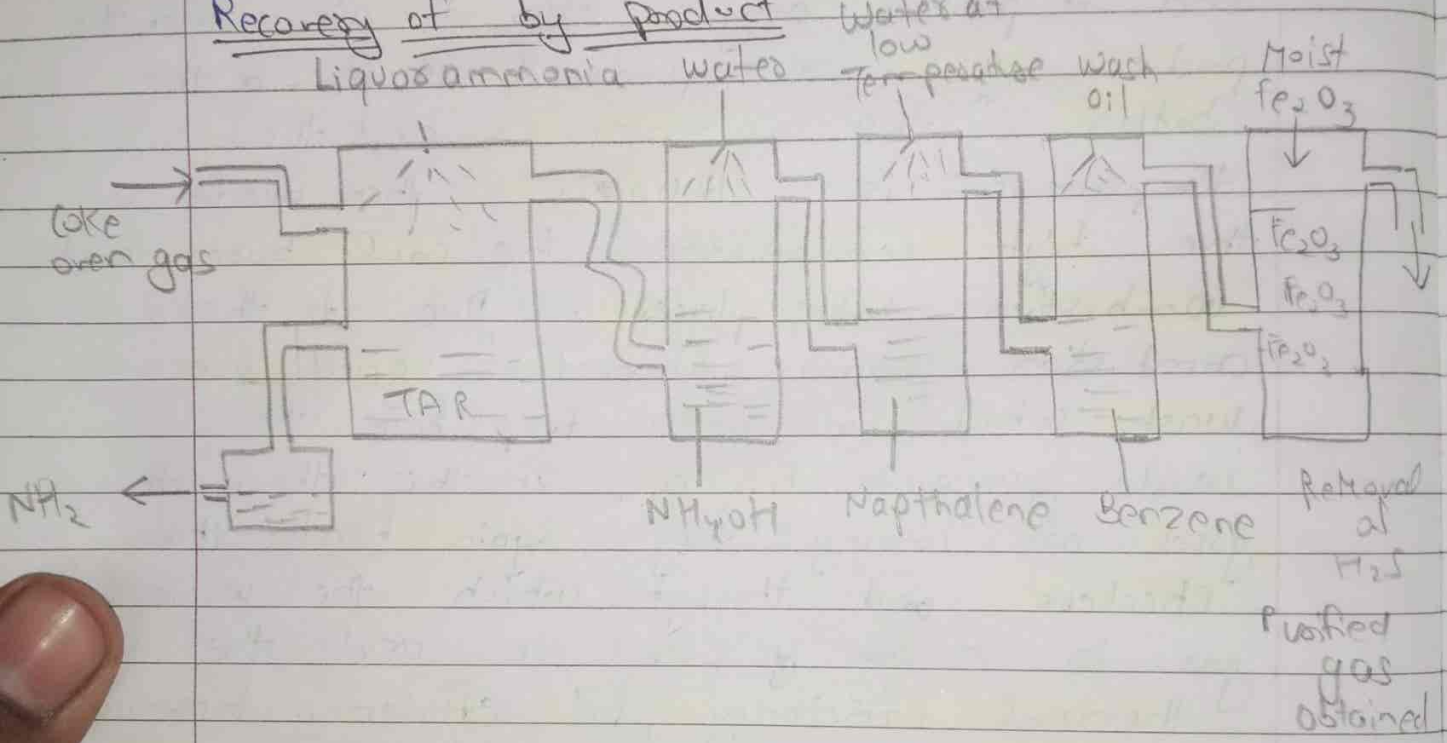
In Dry quenching efficiency is More.

Date

Why Dry quenching is more useful then wet quenching

Dry coke produced during dry quenching is more strong, dense, graphitized, non-reactive, cheaper, contain lessed dust then wet quenched coke

Recovery of by product



The gas coming out from the oven is known as coke oven gas (waste gas)

Recovery of tar → The gas is first passed through a towes in which liquor ammonia is sprayed. Here dust and tar get collected it at a tank below, which is heated by steam coil to recover back ammonia sprayed. The ammonia is used again.

Recovery of ammonia → The gases from the chambers are then passed through a tower in which water is sprayed. Here ammonia reach with water & give NH_4OH Recovery of NH_4OH is important because it blocks all the pipe.

Recovery of Napthalene The gases are then passed through cooling tower in which water at very low temperature is sprayed & napthalene gets recover.

Recovery of benzol The gases are then Sprayed with petroleum and benzene gets recovered.

Recovery of H_2S The gases are then passed into the chamber where Moist Fe_2O_3 are sprayed and Moist Fe_2O_3 react with gases and Sulphur content, H_2S are removed. (Sulphure may form oxide SO_2 and H_2S form H_2SO_4 due to this they corrode all the other thing) after this pure gas are recover.

Purified gas or coal gas or coke oven gas
Coal gas is used as domestic fuel
Main component of coal gas are CH_4, H_2 with small amount of CO_2, CO, N_2

Note: The process of heating coal in the absence of air is known as destructive distillation of coal. Coke, coal tar, coal gas are the byproduct obtained during the destructive distillation of coal

Coking coal → If the residue (coke) obtained after heating is hard, stoong, usable for Metallurgical purpose, the original coal is known as Coking coal.

Caking Coals

Some of the organic component of coal have fusion properties when heated. The ability of coal to Melt on heating and to form a coherent Residue on cooling called Caking coals.

characteristics of Metallurgical coke

Most important industrial fuel is Metallurgical coke. characteristics

1. Calorific value High
2. combustibility easy
3. cost cheap
4. Porosity High
5. Strength Hard & stoong

Liquid fuel

use for Domestic as well as industrial fuel

Better, More efficiency

~~Petr~~

Petroleum → Petro → rock

oleum → Oil

C →	~~80~~ 80 - 87 %
H →	11 - 15 %
S →	0.1 - 3.5 %
O →	0.1 - 0.9 %
N →	0.1 - 4.9 %

Date

~~Refin~~

Process in which petroleum is separated into different fractions having different boiling point is called refining of petroleum

Step 1 → seperation of water or cottrell's process
Step 2 → Removal of sulphur compounds
step 3 → fractional distillation

Refining of Gasoline

unsatrated compound
↓
Gum formation
↓
treating with Soil H_2SO_4

Sulphur compound
Removal of sulphur
↓
Sweeting of petrol

$Na_2PbO_2 + RSH \rightarrow Pb(RS)_2 + NaOH$

$Pb(RS)_2 + S \longrightarrow PbS + RSR$

↙ Mercaptan ↓ Dissulphide compound

Fraction obtain b/w 40°C to 120°C called petrol / gasoline

Sulphur compound (Removal of sulphur)

① gasoline is passed over sodium plumbite

$Na_2PbO_2 + 2RSH \longrightarrow Pb(SR)_2 + 2NaOH$

Mercaptan → lead mercaptide

② Lower Mdecular weight Mercaptides → Insoluble in petrol
Higher " " " → Soluble in petrol

$Pb(SR)_2 + S \longrightarrow PbS + R-S-S-R$

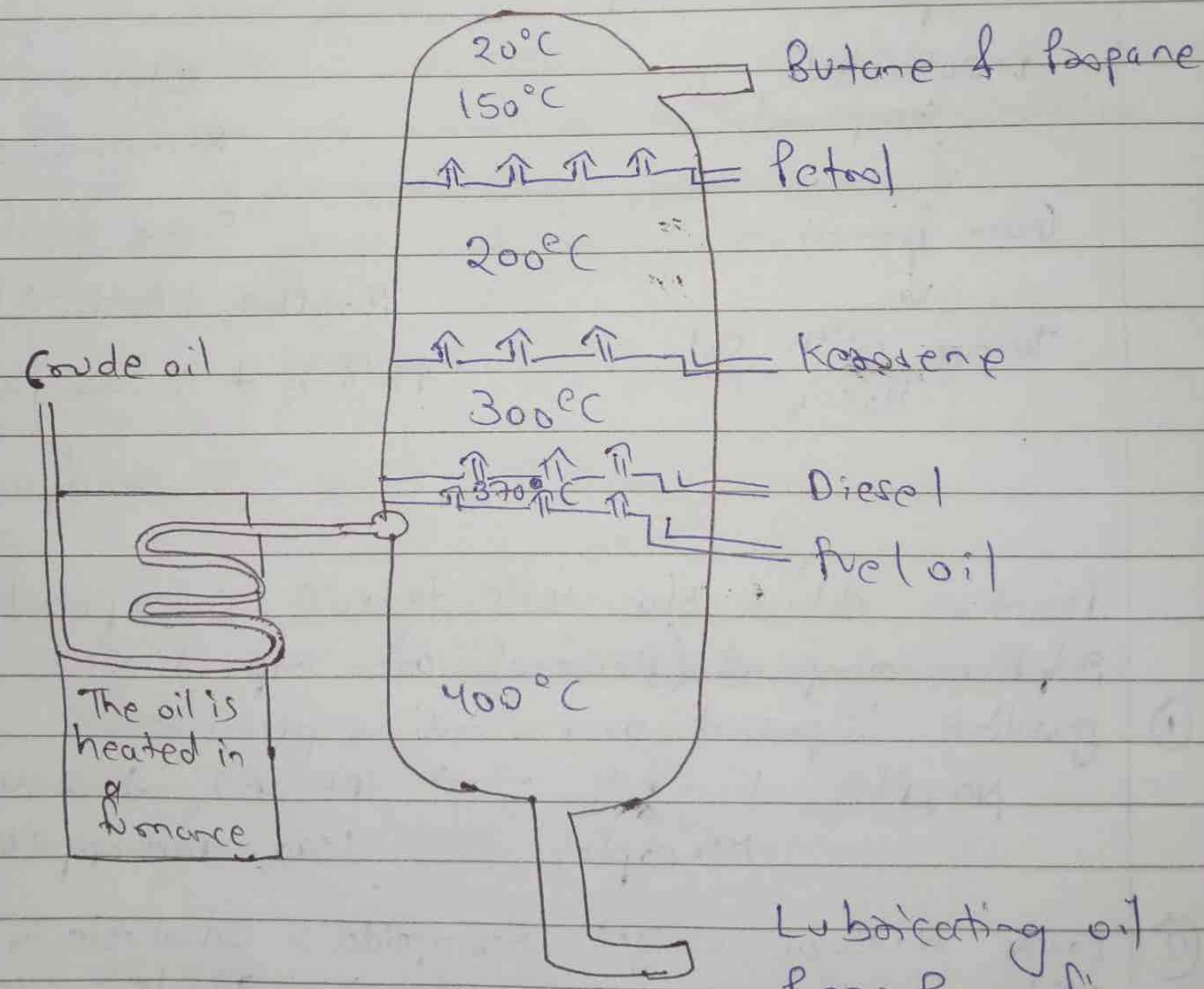
insoluble Mercaptide → bad odour converted → dissulphide which are soluble in petrol & do not have bad odour but still it presence is undesirable

③ gasoline is further refined by vapour phase treatment
④ gasoline free from thio compound

5) Stabilization → gasoline obtained may contain some dissolved gases like Methane, ethane, etc.
These gases are removed by process Stabilization

6) Some inhibitors are added to gasoline to improves its storage quality of gasoline

7) Then it is Mixed with various Anti knocking agents to satisfy its octane no. of petrol.



Petroleum Refining, formation

Cracking → It is defined as the decomposition of high Molecular weight compound having high boiling point into simpler or low Molecular weight compound having low boiling point by application of heat with or without catalyst.

$$C_{10}H_{22} \xrightarrow{\Delta} C_5H_{12} + C_5H_{10}$$

	Decane	Pentane	Petene
BP	174°C	36°C	36°C

Cracking

Thermal
Cracking takes place in presence of heat and pressure

- Liquid phase
  - * Charge in liquid form
  - * Pressure 100 kg/cm²
  - * Temperature 475-530°C
  - * Cracked product separated by fractionating column
  - * Any oil
- Vapour phase
  - * only those oil which can vaporize at low temperature can be cracked
  - * Temperature 670-720°C
  - *

Catalytic

- Fixed bed Catalytic Cracking
- Moving bed catalytic cracking

characteristics	Liquid phase	Vapour phase
Cracking Temperature	475-530°C	620-720°C
Pressure	100 kg/cm²	10-20 kg/cm²
Octane rating of petrol	65-70	>70
Type of oil	Any oil	oil should vaporized
Time required for cracking	More	less

Date

Mechanism of thermal cracking

Thermal cracking is follow by free radical Mechanism

1. Initiation
2. Propagation
3. Termination

Catalytic Cracking

Cracking is done in presence of catalyst at lower temperature and pressure

Catalyst → Mixture of silica + alumina

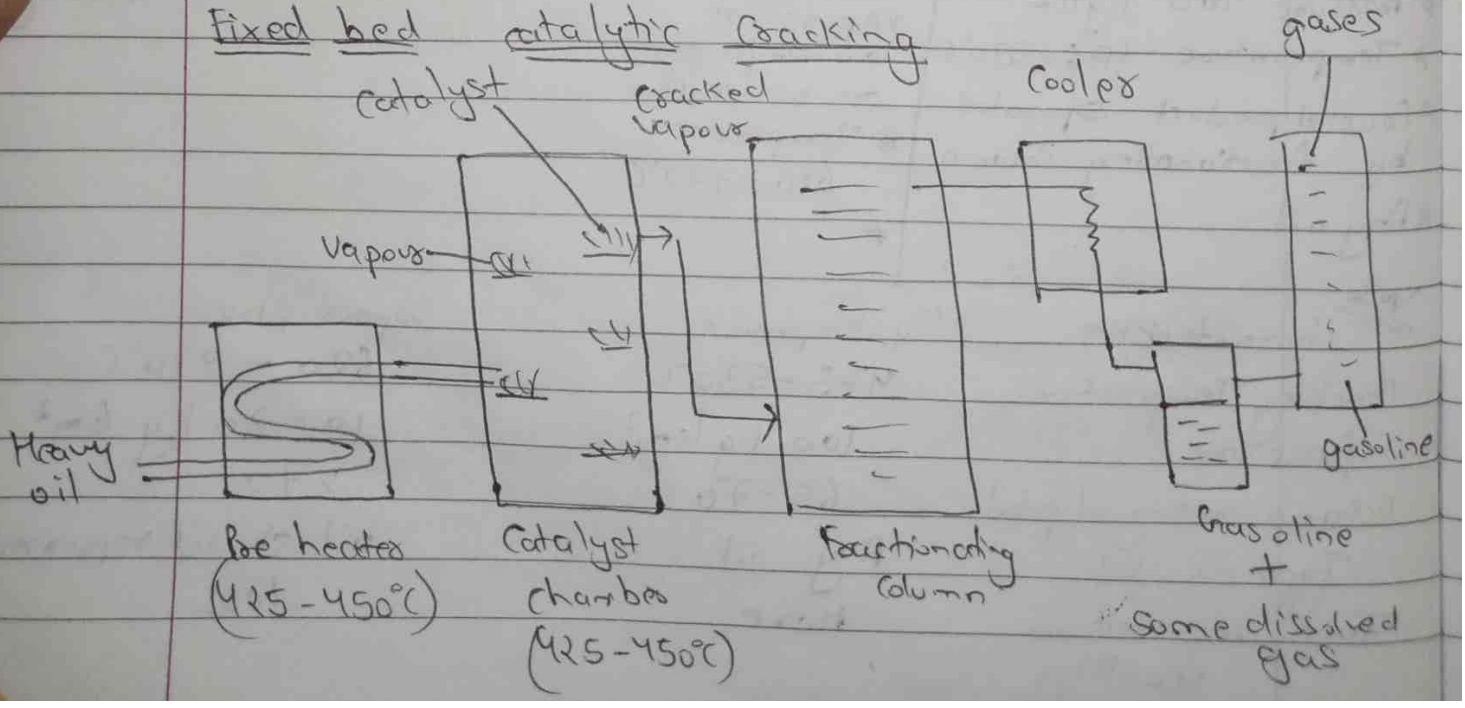
Advantages catalytic cracking over thermal cracking

a) High temperature & pressure are not required in the presence of a catalyst

b) Yield of gasoline is higher about 70% of raw Material is converted into gasoline.

c) Coke forming Material are absorbed by the catalysts.

Fixed bed catalytic Cracking



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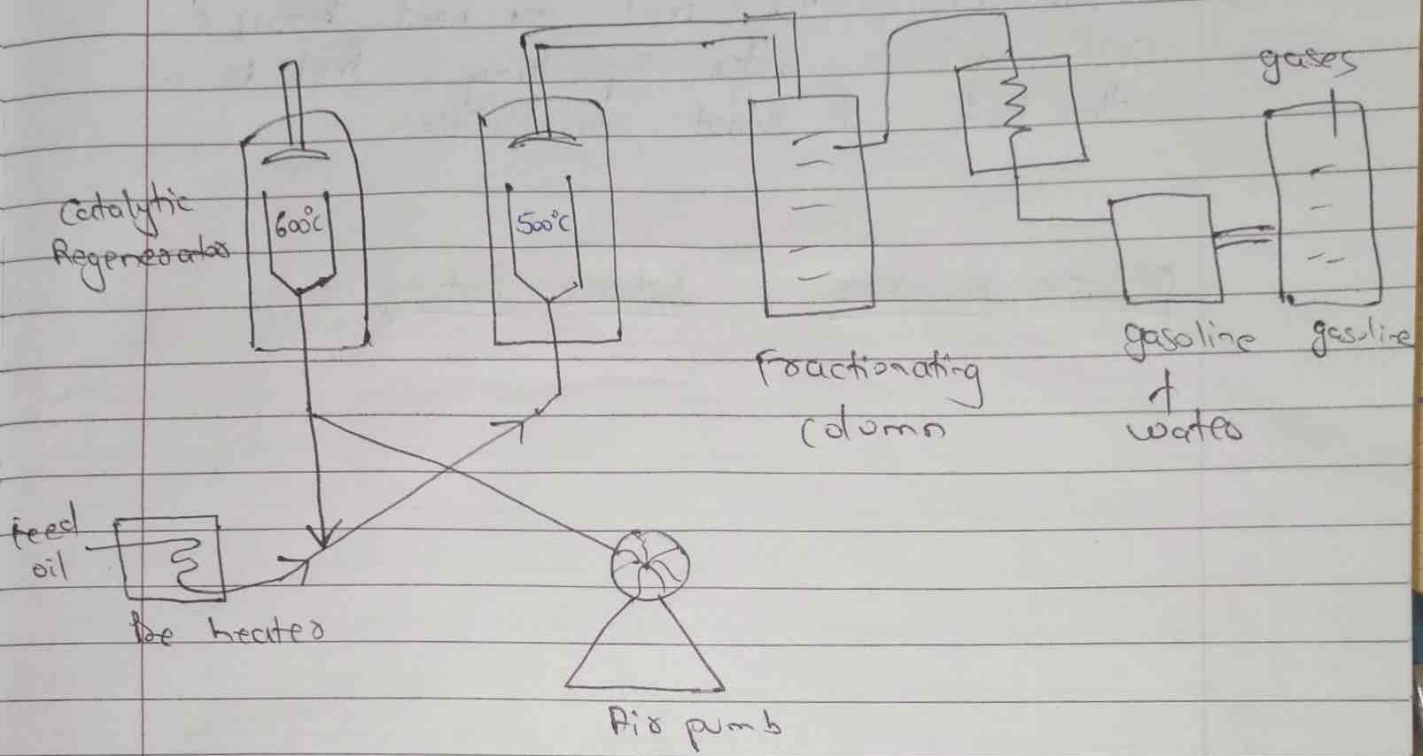
Moving bed catalytic cracking



Knocking

It is the sharp Metallic sound similar to rattling of hammer which is produced in the internal combustion engine due to improper ignition of air / fuel Mixture

★ Knocking ↑ = length of hydrocarbon ↑

n heptane > n hexane > n pentane

★ Knocking ↓ = ↑ compactness of Molecule, double bond, cyclic structure

★ Knocking ↓ = ↑ branched chain isomers

n heptane > 2 Methyl hexane > 2,2 dimethyl Pentane

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Cause of knocking

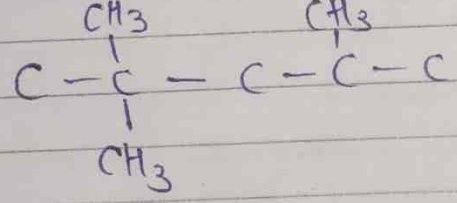
1) Pre ignition → Before sparking → Compression के time में Air & fuel को heat करता है
2) Self ignition after sparking fuel is in the box is start combustion

Octane Number / Octane Rating

Octane Number → It is define as the % of iso octane in the Mixture of iso octane & n-heptane which has the similar knocking characteristics that of the fuel under study under sense set of condition

(2) It is used in Petrol engine, gasoline

Iso octane (2,2,4 trimethyl pentane)



(3) Additive
1. Benzene
2. Tetraethyl lead
3. 1,2 dibromo ethane

(4) Saturated Hydrocarbon (Max)
↓
Branched chain Hydrocarbon
↓
olefine
↓
cyclic hydrocarbon
↓
Aromatics (Min)

→ Knocking decrease as we move down the group
→ Anti knock property increase as we move down the group
→ Octane number of fuel increase as we move downward

Saturated Hydrocarbon > Branched chain Hydrocarbon > define > Cyclic hydrocarbon > Aromatics (Minimum)
(Maximum)

(5) Straight chain Hydrocarbon Molecule are low octane Number

Cetane Rating or Cetane Number

Cetane No → It is the define as the % of hexadecane in the Mixture of hexadecane & 1 Methyl Napthalene which has the Similar knocking characteristics. to that of the fuel under study under same set of Condition.

★ It is used in Diesel engine

★ Aromatics > Branched chain Hydrocarbon > olefine > Napthalenes > n alkane
(Maximum) (least)

Anti Knocking

(5) Straight chain Hydrocarbon Molecule are best, have high cetane Number

Additives
① ethyl Nitrate
② Iso anyl ★ Nitrate

Ignition delay → The combustion of fuel in a diesel engine is not Spontaneous the interval b/w the start of fuel injection and its ignition is called ignition delay.

① Differentiate blw octane No & cetane No
② Straight chain / Long chain hydrocarbon is a good diesel engine but a bad petol engine.

Gaseous fuel

Gaseous fuel obtained
① Nature
② from Solid fuel (producer gas, water gas)
③ from petroleum

Gaseous fuel
1) Natural Gas
2) CNG
3) LPG
4) Coal gas
5) Producer gas
6) Water gas
7) Oil gas

1) Natural gas

Composition → 70 - 90 % of Methane
5 - 10 % ethane
3 % Hydrogen

Uses
a) Domestic fuel
b) Used in the preparation of compressed Natural gas
c) Due to less pollution it is a good substitute of Petrol & diesel
d) used for Manufacture of synthetic chemicals

3) CNG (Compressed Natural gas)
Zero pollution
clean fuel
Environment friendly fuel

3) LPG
Composition → Butane, isobutane, propane
Mixture of gases

Uses
a) ~~Health~~ Not polluted the air
b) LPG Stoves quickly supply heat and work

4) Coal gas
C (in absence of air) → coke + coal gas
Composition → H_2, CH_4, CO, C_2H_2, C_2H_4, N_2, CO_2

Uses
i) Raw Material for ammonia production
ii) Used as a source of light
iii) In Metallurgical operations for providing a reducing atmosphere

5) Producer gas
Composition → CO + N_2

Uses
Manufacture of steel, glass
As a reducing agent in Metallurgical operation

6) Water gas (Blue gas)
Composition → CO + H_2

Uses
used for production of Hydrogen
water gas is used as a fuel in Lonance

7) Oil gas
CH_4, H_2, CO, CO_2

Uses
Used as laboratory gas
Used to improve the calorific value of water

8) Calculate the Minimum amount of air required for the complete combustion of 100kg of fuel containing C = 80%. H = 6%. O = 5%. S = 2% all rest N
Calculate the % of dry product of combustion if 25% excess of air is supplied.

Sol) Step1
Amount of fuel = 100 kg
Step2

comp	weight	chemical react	O_2	dry product
C	80	$C + O_2 \rightarrow CO_2$ (12kg, 32kg)	$\frac{32}{12} \times 80$	
H	6	$2H + \frac{1}{2}O_2 \rightarrow H_2O$	$\frac{16}{2} \times 6$	
O	5			
S	2	$S + O_2 \rightarrow SO_2$	$\frac{32}{32} \times 2$	
N	7			

Total O_2 required $= \frac{32}{12} \times 80 + \frac{16}{2} \times 6 + \frac{32}{32} \times 2$

$= 213.3 + 50$

$= 263.3$

we will Minus O_2 given

$$263.6 - 5 = 258.3 \text{ kg}$$

Air required $= \frac{258.3}{23} \times 100$

$$= 1123.04 \text{ kg}$$

b) Excess air wala $= 1123.04 \times \frac{125}{100}$

$$= 1403.8 \text{ kg}$$

Dry product composition

12 kg of C → 44 kg of CO_2

80 kg of C → $(\frac{44}{12} \times 80)$ kg of CO_2

Amount of O_2 → according to $\frac{44}{12} \times 60$

Amount of SO_2 → $\frac{64}{32} \times 2$ kg

Amount of $O_2 = \frac{23}{100} \times 280.79$ (25% excess wala)

Amount of $N_2 = \left[\frac{77}{100}(1403.8) + 7\right]$ kg

=

Total dry product

$$\Rightarrow \frac{44}{12} \times 60 + \frac{64}{32} \times 2 + \frac{23}{100} \times 280.7 + \frac{77}{100} \times 1403.8 + 7$$

$$= 1449.79 \text{ kg}$$

Date

$$\% CO_2 = \frac{\text{Amount of } CO_2}{\text{Total wt of dry product}} \times 100$$

Similarly

% SO_2 " "
% O_2 " "
% N_2 " "

(23) A gaseous fuel of $1\ m^3$ has the following composition by volume

$CH_4 = 4\%$
$CO = 26\%$
$H_2 = 10\%$
$N_2 = 50\%$

If 20 % excess air is supplied calculate the actual volume of air supplied.

21% → O_2 (by volume)
79% → N_2

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Sol) Amount of fuel = $1 m^3$

Components	Amount	chemical reaction	Amount of O_2 required (m^3)
CH_4	$\frac{4}{100} \times 1 = 0.04 m^3$	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	0.04×2
CO	$\frac{26}{100} \times 1 = 0.26 m^3$	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	$0.26 \times \frac{1}{2}$
H_2	$0.1 m^3$	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$0.1 \times \frac{1}{2}$
N_2	$0.5 m^3$		

Minimum O_2 required = $0.04 \times 2 + 0.13 + 0.05$
= $0.26 m^3$

Minimum air required = $\frac{100}{21} \times 0.26 = 1.23 m^3$

Excess air = $\frac{20}{100} \times 1.23 \ m^3$

Actual air Supplied = $1.23 + 0.24$
= $1.47 m^3$

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Unit 2

Phase → A phase is a homogenous, physically distinct and Mechanically Separable part of a system which is separated from other part of the system by definite boundaries.

Example

1) One phase System
A gaseous Mixture, being thoughly Miscible in all proportion constitutes one phase only.
Example → A Mixture of N_2 & H_2 forms one phase only.
Two Miscible liquids (eg water & alcohol) constitute one phase only
A Solute completely dissolved in a solvent constitutes a single phase.
like salt in water. (Mohr's Salt)

2) Two phase System
If two liquid are immiscible eg (oil & water) they will constitute two Separate phases.
ex) benzene & water.

3) Three phase System

At freezing point water consist of three phases

$$\text{Ice (s)} \rightleftharpoons \text{Water (l)} \rightleftharpoons \text{Water vapour (g)}$$

When $CaCO_3$ is heated in closed vessel, it decompose into CaO and CO_2 at equilibrium there are two solid and one gaseous phase so it is three phase System

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$(s) \qquad (s) \quad (g)$$

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VVI $Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g)$

There are two solid phases Fe and FeO and one gaseous phase consisting of $H_2O(g)$ and $H_2(g)$. Thus they are <u>three phase</u> exist in equilibrium

VVI

Q) Identify No. of phase

1) A bottle containing aqueous Sol^n of ammonium hydroxide

Ans) 1

2) Ether and water contained in stoppered flask

Ans) 2

3) A mixture containing powdered sulphur, sugar and urea

Ans) (Three) 3

4) Sulphur system $S_R = S_M = S_L = S_V$

Ans) 4

5) An aqueous solution of glucose

Ans) 1

6) Mixture of N_2 & O_2

Ans) 1

<u>Component</u>

It is defined as the smallest number of independently variable constituent of equilibrium by means of which the composition of each phase present can be expressed either directly or in the form of a chemical reaction

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Ex→
One component System
a) Ice (s) = water (l) = water vapour (g)
It is a three phase
but the all has a same chemical component H_2O so they are one component System
b) S(R) = S(M) = S(L) = S(V)
phase 4
same Sulphur composition so it is one component System

Two component System
$CaCO_3(s) = CaO(s) + CO_2(g)$
3 Phase (two solid + 1 gases)
but it is a two component system
$CaCO_3$ solid phase $CaCO_3 = CaCO_3 + 0\ CaO$
CaO solid phase $CaO = 0\ CaCO_3 + CaO$
CO_2 gaseous phase $CO_2 = CaCO_3 - CaO$
Here only two component are required to express the composition of each phase it is a two component System or binary System

$MgCO_3 = MgO(s) + CO_2(g)$

Calculation of No. of components

a) $\boxed{C = S - R}$ when No ions present

C → Component of System
S → Substances or No. of Constituent
R → is the relation (No of equations relating to these constituent in an equilibrium state

b) $C = S - [R+I]$

When ions are also present in the system then the condition of electroneutrality (No of the +ve charges should be equal)

Q1) Predict the No. of component for dissociation of $KClO_3$ in a closed vessel (Same for $CaCO_3$, $MgCO_3$)

Sol) $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$

$R = 1$ (1 equ only), $S = 3$

$C = S - R$

$= 3 - 1 = 2$

Ans) 2

Q2) Predict No of component for dissociation of NH_4Cl on being heated alone in a closed system

Sol) $NH_4Cl \rightleftharpoons NH_3 + HCl$ — (1)

$[NH_3] = [HCl]$ — (2)

$R = 2$ $S = 3$

$C = S - R = 3 - 2 = 1$

It is two Phase

Ans) 1

Q3) Predict the no of component when NH_3 and NH_4Cl is heated in a closed vessel along with HCl

Sol) $NH_4Cl \rightarrow NH_3 + HCl$ — (1)

$[NH_3] \neq HCl$ — (2)

$R = 1$, $S = 3$

$C = 3 - 1 = 2$

Ans) 2

Q4) $CaCO_3(s)$, $CaO(s)$ $CO_2(g)$ When CaO and CO_2 in the system are formed exclusively by decomposition of $CaCO_3$

Sol) $CaCO_3 = CaO + CO_2$ $R = 1$

$C = 3 - 1$ $S = 3$

$C = 2$ Ans

Q) Explain why $KCl - NaCl - H_2O$ should be regarded as a three component system whereas $KCl - NaBo - H_2O$ should be regarded as two component system.

Sol) $KCl - NaCl - H_2O$

$[KCl, NaCl, H_2O, K^+, Na^+, Cl^-]$ $S = 6$

$NaCl \rightarrow Na^+ + Cl^-$

$KCl \rightarrow K^+ + Cl^-$

$R = 2$

$C = S - [R+I]$

$= 6 - [2+1] = 3$

$KCl - NaBo - H_2O$

$[KCl, NaBo, H_2O, K^+, Na^+, Cl^-, Bo^-, KBo, NaCl]$

$S = 9$

$NaCl \rightarrow Na^+ + Cl^-$

$KCl \rightarrow K^+ + Cl^-$

$K^+ + Bo \rightarrow KBo$

$Na^+ + Cl^- \rightarrow NaCl$

$R = 4$

$C = 9 - (5) = 4$

Proved

Degree of freedom (Variance)

The minimum no. of independent variable (such as temperature, pressure and composition of the phase) which must be specified in order to define the system completely is called degree of freedom

Ex → Ice $\rightleftharpoons$ water $\rightleftharpoons$ vapour $F = 0$

If $F = 0$ system is invariant or Non variant

If $F = 1$ system is univariant or Monovariant

If $F = 2$ system is bivariant, $F = 3$ System bivariant

Phase Rule → Phase rule enables us to predict the condition that must be specified for a system to exhibit equilibrium

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Gibbs Phase Rule

$P + F = C + 2$

$F = C - P + 2$

No of degree of freedom — F; No of component — C; No of phases — P

In Reduced Phase Rule If one variant fixed
$P + F = C + 2 - 1$
if two fixed
$P + F = C + 2 - 2$

Q) Calculate F

a) Solid Iodine in equilibrium with its vapour

Sol) $I_2 (s) \rightleftharpoons I_2 (v)$

$F = C - P + 2$
$= 1 - 2 + 2$
$= 1$

b) NH_3 at 42°C

$F + P = C + 2 - 1$ (because on 42°C given)
$F + P = C + 1$
$F + 1 = 1 + 1$
$F = 1$

Phase diagram for water system (one component system)

$C = 1$
$P = 1$ (Minimum phase)
$F = C - P + 2$
$= 1 - 1 + 2$
$= 2$

Minimum $F = 0$
$F = C - P + 2$
$0 = C - P + 2$
$0 = 1 - P + 2$
$P = 3$

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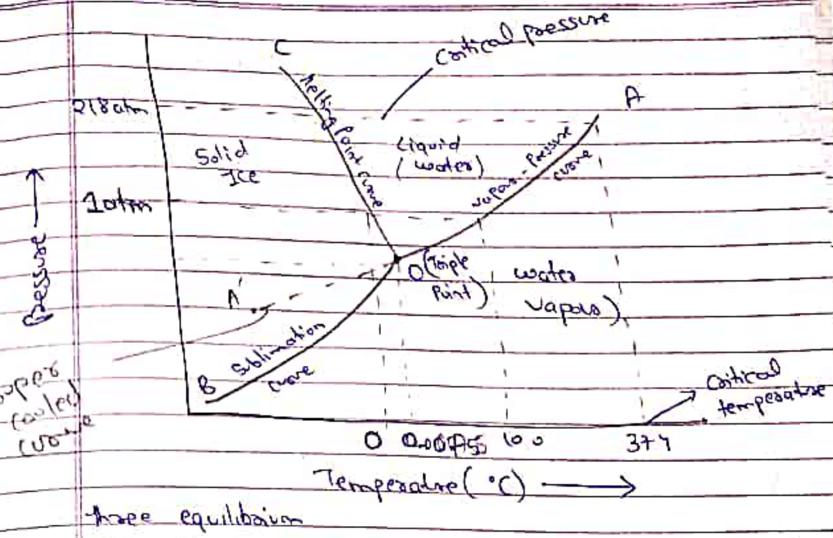

Three equilibrium
Solid ⇌ liquid
Solid ⇌ gas
Liquid ⇌ gas

Sublimation → Solid to gas directly

Critical temperature → इस temperature के बाद वह अपनी state change नहीं करेगा
Critical pressure

Triple point → is a point जिस पर पानी की तीनों phases एक साथ exist कर सकती हैं।

OA curve $F = C - P + 2$
$F = 1 - 2 + 2 = 1$

OB curve $F = C - P + 2$
$= 1 - 2 + 2 = 1$

OC curve $F = 1 - 2 + 2 = 1$

Metastable equilibrium at 0°C water change its state and become freezen

पानी को 0°C से कम temperature पर cool करेंगे called super cooled water

at Triple point O = $F = C - P + 2$
$= 1 - 3 + 2 = 0$

ऊपर रखा Ice का Piece and ... तो अपनी equilibrium change होगा called meta

Phase Rule
water system
sulphur System

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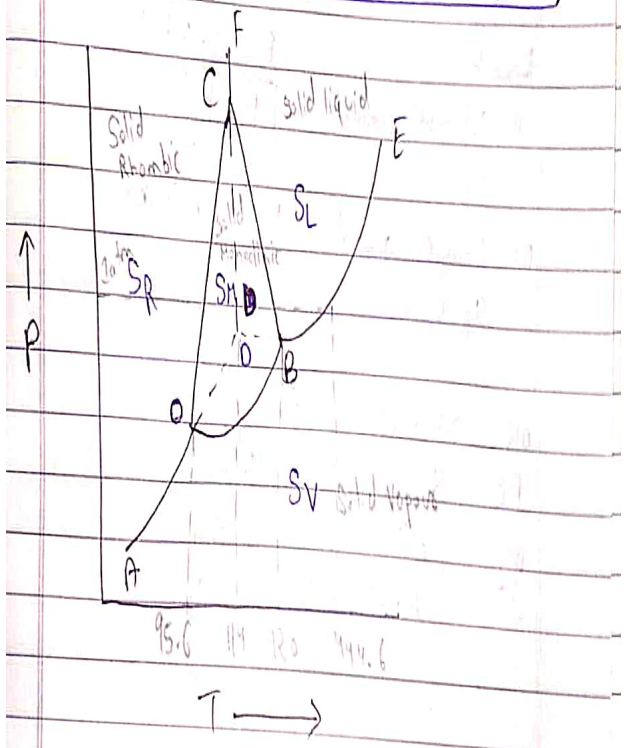
One component System
water System

Sulphur System

$S_R \gtrless S_M \gtrless S_L \gtrless S_L$

S S S S

C=1 because one component system है



Area (A)	Curve	Point
AOCF, COBC	OA, OB, BE	O, B, C
FCBE, AOBE	OC, BC, CF	O

C=1, P=1 (एक area में है)

$F = C - P + 2$

$F = 1 - 1 + 2 = 2$

F=2

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for curves

OA ⇒ $S_R \rightleftharpoons S_V$ — equilibrium represents

OC ⇒ $S_R \rightleftharpoons S_M$
OB ⇒ $S_M \rightleftharpoons S_V$
BE ⇒ $S_L \rightleftharpoons S_V$
BC ⇒ $S_M \rightleftharpoons S_L$
CF ⇒ $S_R \rightleftharpoons S_L$

these are represents the equilibrium b/w the two phases.

$C=1 \quad P=2$ (Two area)

$F = C-P+2$
$F = 1-2+2$
$\boxed{F=1}$
it is univariant

here
OA = Sublimation curve of S_R
OC = Transition curve of S_R to S_M

OB = Sublimation curve of S_M
BE = Vapour pressure curve
BC = Melting curve of S_M
CF = Melting curve of S_R

for points

O, B, C, D — $C=1$, $P=3$, $F = 1-3+2 = 0$ — for O, B, C — triple point

O	$S_R \rightleftharpoons S_M \rightleftharpoons S_V$	95.6°C	0.06 mm
B	$S_M \rightleftharpoons S_L \rightleftharpoons S_V$	120°C	0.04 mm
C	$S_R \rightleftharpoons S_M \rightleftharpoons S_L$	151°C	1288 atm

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Point D

S_R | S_L
D
S_V

→ Metastable ~~point~~ Triple point
114°C & 0.03 mm of Hg

Two component System

$F = C-P+2$ Put $C=2$
$F = C-P+2 = 2-P+2 = 4-P$
if $P=1$
$\boxed{F=3}$ P, T, C

$\boxed{F = C-P+2}$ for one ~~phase~~ component system

$\boxed{F = C-P+1}$ for two component system

~~this is called Condensed phase rule~~
Reduced phase rule

Solid ⇌ liquid ⇌ Reduce of System
condensed System

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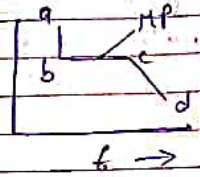
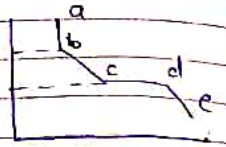
Cooling Curve

i) Pure Substance



ii) Mixture of Substance



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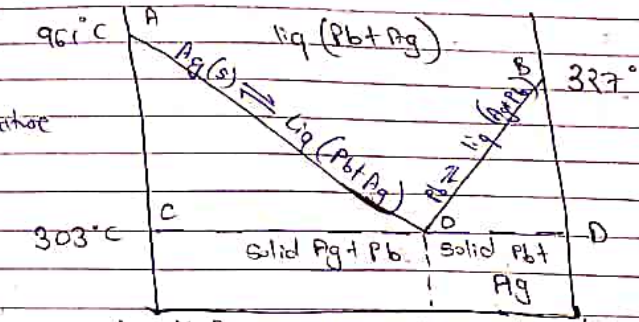
Two component System

Lead Silver System (Pb-Ag System)



Areas	Curves	Points
Above AOB	OA	A
Below line AO & OB	OB	B
Below line COD		O

A point is Melting point of silver (Ag) at 961°C

B point is Melting point of lead (Pb) at 327°C

O point is Eutectic point (below O all component solidify)

Area AOB P=1 C=2

$F = C - P + 1 = 2 - 1 + 1 = 2$

Area below line AO & OB

AO $Ag(s) \rightleftharpoons liq(Pb + Ag)$

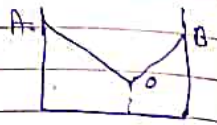
BO $Pb(s) \rightleftharpoons liq(Pb + Ag)$

$F = C - P + 1 = 2 - 2 + 1 = 1$

Curve
OA $Ag(s) \rightleftharpoons liq(Ag + Pb)$
OB $Pb(s) \rightleftharpoons liq(Pb + Ag)$

$F = C - P + 1$
$= 2 - 2 + 1$
$F = 1$

Area below COD
$P = 2$ [Ag(s) + Pb(s)]
$C = 2$, Ag , Pb
$F = C - P + 1$
$F = 2 - 2 + 1 = 1$



Point O (has lowest Melting point)
Eutectic Point
Temp = 303°C

$C = 2$ $P = 3$
$Ag(s) \rightleftharpoons Pb(s) \rightleftharpoons liq(Pb + Ag)$

$F = C - P + 1$
$F = 2 - 3 + 1 = 0$

Composition (97.4% Pb , 2.6% Ag)

Eutectic point → Two curve AO & BO intersect at point O at Temp 303°C This point is known as eutectic point.

Desilverization of anti ferrous Lead
(Pattinson's Process)

Eutectic System A binary System consisting of two substances which are miscible in all proportion in the liquid phase & do not react chemically.

Eutectic Mixture → The two substance involved have the property of lowering each other freezing point. Solid sol" of two or more substance having the lowest freezing point of all the possible Mixture of the component is known as Eutectic Mixture.

The process of heating argentiferous lead containing a very small quantity of Ag (0.1%) and cooling it to get pure lead and liquid rich in silver is called Pattinson's Process

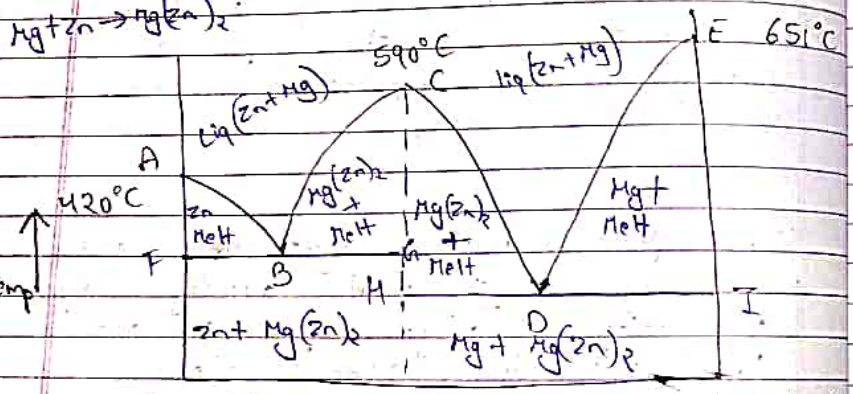
Two component chemical reaction

No → Eutectic System
(Miscible in all proportion)
Pb - Ag

Yes → Congruent compound (Same composition) (Zn - Mg)
Incongruent compound (Different composition in both phase) (Na - K)

Zn - Mg System

$Mg + Zn \rightarrow Mg(Zn)_2$



Zn = 100%
Mg = 0%

Mg = 100%
Zn = 0%

Composition →

Points

A → MP of Zn 420°C
C MP of $Mg(Zn)_2$ 590°C
E MP of Mg → 651°C

} C = 2, P = 2, F = 2-2+1 = 1

B Eutectic point 347°C

$Zn(s) \rightleftharpoons Mg(Zn)_2(s) \rightleftharpoons liq\ (Zn+Mg)$

C = 2 P = 3 F = 2-3+1 = 0

D → Eutectic Point 347 °C

$Mg(s) \rightleftharpoons Mg(Zn)_2 \rightleftharpoons Melt\ (Mg+Zn)$

Curve (Univariant)

AB $Zn(s) \rightleftharpoons liq\ (Zn+Mg)$
BC $Mg(Zn)_2 \rightleftharpoons liq\ (Zn+Mg)$
CD $Mg(Zn)_2 \rightleftharpoons liq\ (Zn+Mg)$
DE $Mg(s) \rightleftharpoons liq\ (Zn+Mg)$

C = 2 P = 2
F = C - P + 1 = 2 - 2 + 1 = 1

Area

ABFA
BGCB
CHDC
EDIE

} P = 2 C = 2 F = 2-2+1 = 1

Area above ABCDE P = 1 C = 2 F = 2-1+1 = 2

Area below FBGHDI

C = 2 P = 2
F = 2 - 2 + 1 = 1

freedom

Date : / /
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Polymer

Poly mer
Many Parts/unit

Mono mer
Single Part/unit

It is composed a large no. of repeating unit of identical structure called Monomer. (Combination or large chain of Monomer forms polymer)

e.g.)

$$n\,CH_2 = CH_2 \longrightarrow -(CH_2 - CH_2)-$$

ethene — Monomer

Polyethene — Polymer

Polymer

Natural: Cellulose, Protein, Silk

Synthetic: Nylon, plastics

Degree of Polymerization The no. of repeating units in a chain formed in a polymer is called degree of Polymerization.

Degradation of Polymer (Breakdown of Polymer)
Breakdown of Polymer by heat called Thermal degradation if by water it is called Hydrolytic degradation
if by Microorganism it is called Biodegradation
if by light it is called photo degradation
if by oxygen is called Oxidative degradation

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Environmentally Biodegradable Polymer
A polymer based on the C-C backbone tends to be Non biodegradable where as hetero atom containing polymer backbones confer biodegradability.

Biodegradable Polymers Degradation Caused by Biological activity (Microorganisms)

Example a) (PHB) poly hydroxy butyrate
b) (PVOH) poly vinyl alcohol
c) PLA Poly Lactic acid

Classification of Polymer

1) On the Basis of origin

Natural	Semisynthetic	Synthetic
Starch	ex-> Rayon	PVC, Nylon
Protein		Polyethylene
Cellulose		etc

2) On the basis of chemical Structure

Homopolymer
Consist same Monomer
ex-> Vinylchloride -> PVC
ethylene -> Polyethylene

Co polymer
or
Hetro polymer
Consist More than one type of Monomer

3) On the Basis of polymeric Structure

Linear polymer
High density
-A-A-A-A-

Branced polymer
low density
A-A-A-A
A' A'

Cross linked polymer
Network
A-A-A-A-A-A
A-A B' A-A-B'-A
A' A'

Nylon 6,6

4) On the Basis of Thermal Behavior

Thermoplastic — Thermosetting

Mechanism of Polymerization

① Additive Polymerization ② Condensation Polymerization

1) Free radical addition polymerization

Step1 chain initiation

$$I_2 \longrightarrow 2I^{\bullet}$$

$$I^{\bullet} + CH_2 = CH_2 \longrightarrow I-CH_2-CH_2^{\bullet}$$

Step2 chain propagation

$$I-CH_2-CH_2^{\bullet} + CH_2=CH_2 \longrightarrow ICH_2-CH_2-CH_2-CH_2^{\bullet}$$

$$+ CH_2=CH_2$$

(PE)

Step3 chain termination

$$ICH_2-CH_2-CH_2CH_2^{\bullet} + {}^{\bullet}CH_2CH_2CH_2CH_2I \longrightarrow ICH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2I$$

2) Ionic Mechanism (cationic or anionic)
3) Coordination Mechanism
(In the presence of organometalic compound (as Ziegler Natta catalyst)

Polymer Functionality

The No of reactive sites in a Molecule is termed as functionality

for Molecule to act as Monomer it must have at least two reactive sites then its functionality should be two

example

a) $CH_2 = CH_2 + H_2 \longrightarrow H - CH_2 - CH_2 - H$

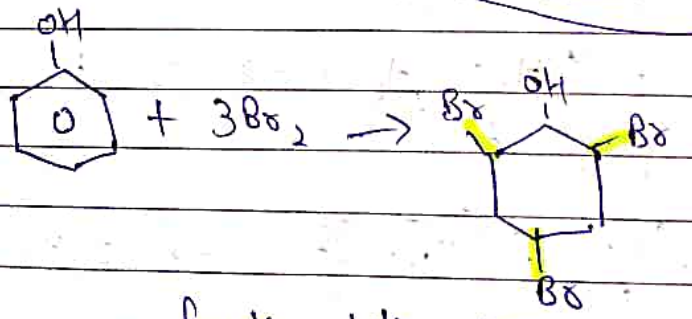
Here $-CH_2 - CH-$

functionality = 2

b) $CH \equiv CH + 2Cl_2 \longrightarrow Cl-\underset{Cl}{CH}-\underset{Cl}{CH}-Cl$

functionality = 4 $-CH-CH-$

c)



functionality = 3

Note Monomer has functionality = 2 it is linear polymer

Monomer has functionality = 3 it is Cross linked polymer

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Molecular weight of polymer

Two ways

① Number average Molecular weight (M_n)

$n_1 n_2 n_3$ - - are No of Molecules & Molecular Mass $M_1 M_2 M_3$ - - -

$$\overline{M_n} = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 - - -}{n_1 + n_2 + n_3}$$

$$= \frac{\text{Total Mass of Polymer}}{\text{Total No. of Molecules}}$$

② Weight average Molecular weight

If $m_1 m_2 m_3$ - - - are weight of ~~Mo~~ species

$M_1 M_2 M_3$ - - - ~~wt~~ Molecular Mass

$$M_w = \frac{m_1 M_1 + m_2 M_2 + m_3 M_3}{m_1 + m_2 + m_3}$$

Polyethylene (Addition Polymers)

Polyethylene also known as polyethene, it is important thermoplastic resin ~~propa~~ prepared by the addition polymerization of ethylene.

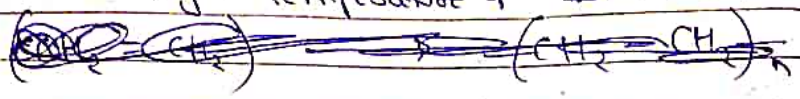
Types

a) Low density polyethene (LDPE)
b) High density polyethene (HDPE)
c) Linear low density polyethene (LLDPE)
d) Ultrahigh Molecular weight polyethene (UH MWPE)

A) Low density polythene (LDPE)

Preparation

High Temperature & ~~Low~~ Pressure



$$n\,H_2C=CH_2 \xrightarrow{350-570\,K,\ 1000-2000\,atm} -(H_2C-CH_2)_n-$$

ethene Monomers — Free Radical Mechanism — Polyethene

Property	Uses
a) Low density	a) Soft Toys
b) Weak intermolecular force	b) Squeeze bottles
c) chemically inert	
d) Branched	
e) Soft	

2) High density polythene (HDPE)

Preparation

It can be obtained ~~for~~ in ethene Monomers by using Zeigler Natta catalyst ($TiCl_4$ + AlR_3) ~~low temperature & pressure~~

$$n\,H_2C=CH_2 \xrightarrow[\text{Zeigler Natta Catalyst}]{333-343K,\ 5-7\,atm} -(H_2C-CH_2)_n-$$

ethene Monomers — Polythene

Property	Uses
a) Hard	(1) Bucket
b) High density	(2) Dustbins
c) Unbranched	(3) Bottles, pipes

c) LLDPE (Linear low density polyethylene)

It is actualy a copolymer of ethylene and 1 butene manufactured with ziegler type catalyst

LLDPE is attractive because it requires less energy to produce than LDPE

Uses

a) Golf ball Cover Making
b) Bottles

d) UHMWPE (ultra high Molecular - weight polyethylene)

UHMWPE sheet is cut into small block to be used as a brake

UHMWPE is a successful bio material for use in hip knee

UHMWPE is used for Manufacturing of Hydraulic seals

It is used in Making ~~Surgical~~, Machine parts.

Polymer Synthesis

① Condensation polymerization
② Addition Polymerization

① Condensation polymerization

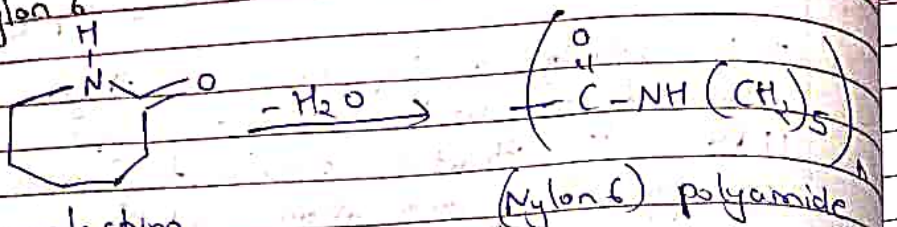
→ For condensation polymerization Monomers should have at least two functional groups Both functional group May be same or not

→ Monomers having two functional groups always give linear polymer

→ Monomer having three functional group always give cross linked Polymer

★ All resins are cross linked polymer & all cross linked polymer are condensation polymers.

2) Nylon 6



Caprolactum

(Nylon 6) polyamide

Same type of Monomers combined togethes called Homo polymerization (Self polymerization)

→ Removal of water Molecule

→ Six Carbon atom present in the Monomer So this polymer is called Nylon-6

→ It is used for Manufacture of tyre cords and ropes

3) Nylon 66

$$n\,H_2N-(CH_2)_6-NH_2 + n\,HOOC-(CH_2)_4-COOH$$

Hexa Methylene diamine

$$\downarrow$$

$$n H_2O + \left(N-(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right)_n$$

Polyamide (Nylon 66)

If different types of Monomers combined bgether called copolymerization with the elemination of H_2O

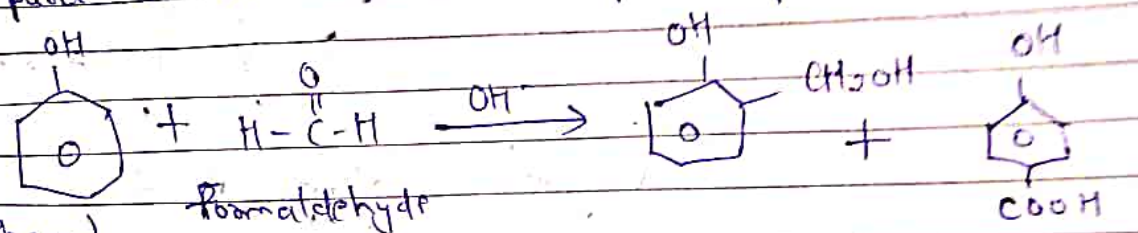
Both Monomers have 6 carbon atom so it is Nylon 66

Uses → Sheets, brushes, textiles

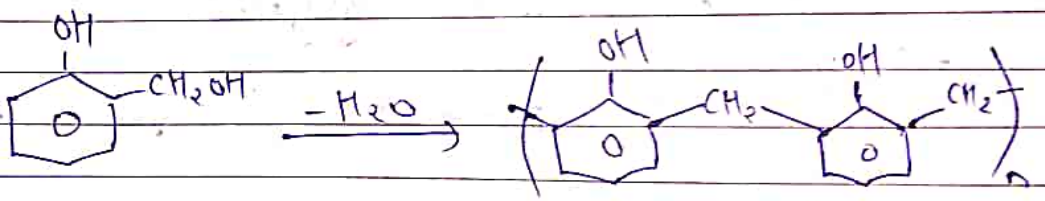
c) Phenol - formaldehyde resin (Bakelite)

→ Starting material is Phenol and formaldehyde in the presence of basic catalyst they two combine & give ~~either~~ ortho & para hydroxy Methyl phenol.

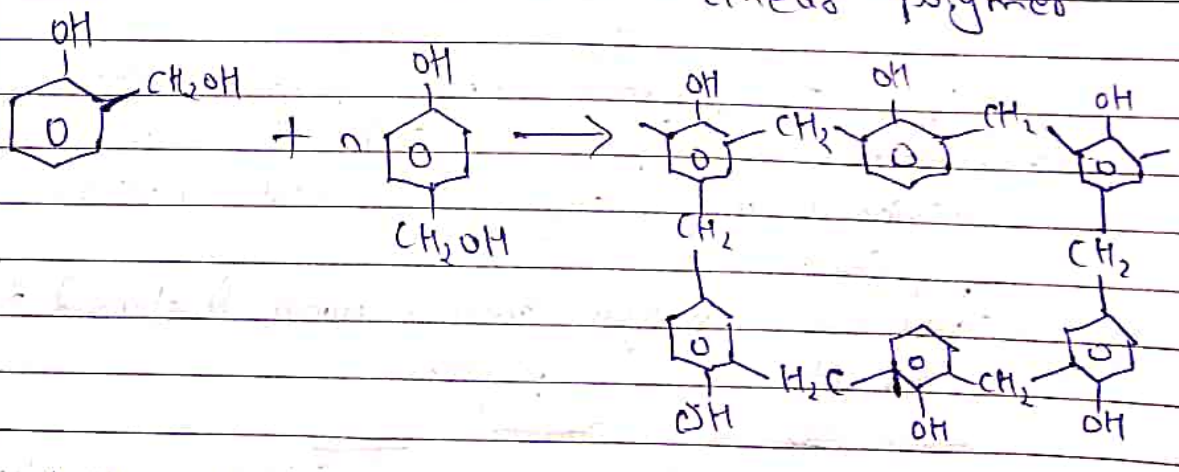
→ This ortho para hydroxy Methyl phenol go condensation to produce cross linked polymer bakelite involving Methylene bridges in ~~the~~ para or both ~~&~~ ortho & para position.



Now



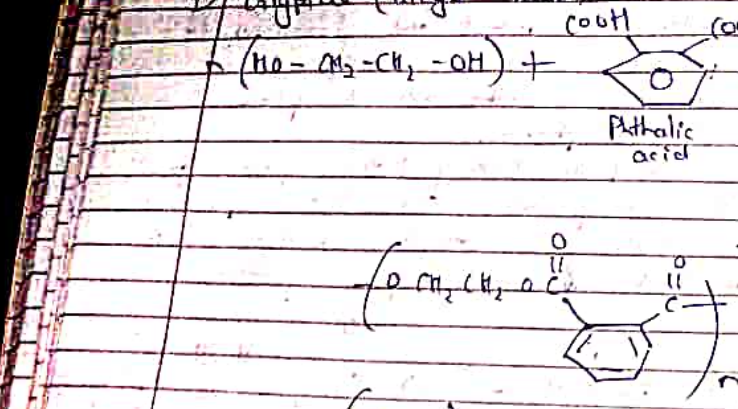
linear polymer



Phenol formaldehyde resin (Bakelite)

Cross linked polymer

4) Glyptal (Alkyd Resin)



(Polyester) glyptal Resin

→ Copolymerization condensation with elemination of H_2O form glyptal

→ uses

① Manufacture of paints

Speciality Polymers

Speciality polymers are polymers having properties and characteristics specially designed for engineering and Medical purposes

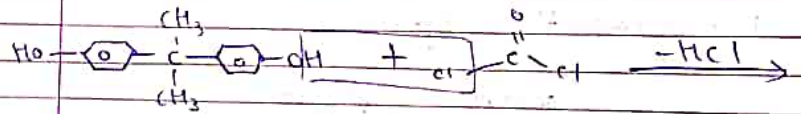
They are ranged from Mono functional to Multifunctional polymers.

~~Main classes are~~ Uses

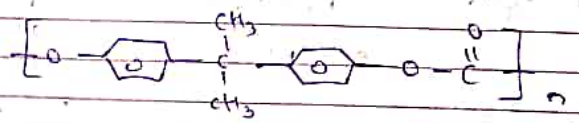
1) It is used in automobile idustry for Making Motorcycle, Safety helmets etc.
2) It is used for Making furniture, camera etc
3) Due to its temperature resistance, Stability and chemical inertness it finds use in Manufacturing of Baby bottles etc
4) It is used for Moulding, for computers, CDs, DVD, hair driers etc

5) Polycarbonate or (engineering thermoplastics)

commonly known as Lexan or Merlon obtained by reacting Bisphenol A with diphenyl Carbonate or Carbonyl chloride



Bisphenol A Carbonyl chloride



Poly carbonates

Properties

a) High impact Strength
b) Highly transparent (about 88%)
c) Good heat resistant
d) Low combustibility
e) High Melting point
f) Good thermal Stability

Application

1) Data Storage
2) Electrical and electronic components
3) Construction Material

3) Conducting polymers
Some polymers have been synthesised which have high planarity and conjugation of $\pi e^{\ominus}$ s. these polymers are known as conducting polymers.

Application
i) In rechargable light weight batteries
ii) In transistor, photodiodes & LEDs
iii) Used in photovoltaic devices
iv) use in solar cells
v) telecommunication systems

Conducting polymers

Aromatic cycle	Double bond	Aromatic cycle and double bonds
	ex) PAC	ex) PPV

Absence Heteroatom
ex) poly fluorenes

Nitrogen containing
ex) PPY

Sulfur containing
ex) PT
PEDOT

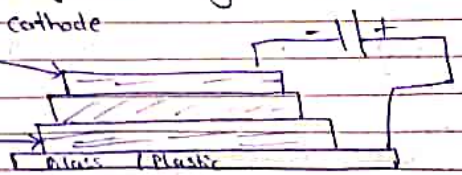
Polyacetylene  Conductivity 10^5

3) Electroluminescent Polymers
Electroluminescance is a phenomena in which a material emit light in response to the passage of an electric current or strong electric field

ex) PPV (Polyphenylene vinylene)
These polymers are used in LED

Polymer Light Emitting diode (PLED)

Calcium (act as cathode)

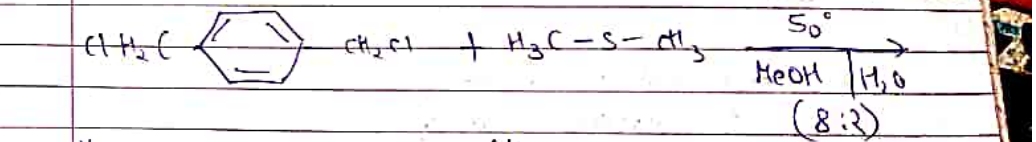


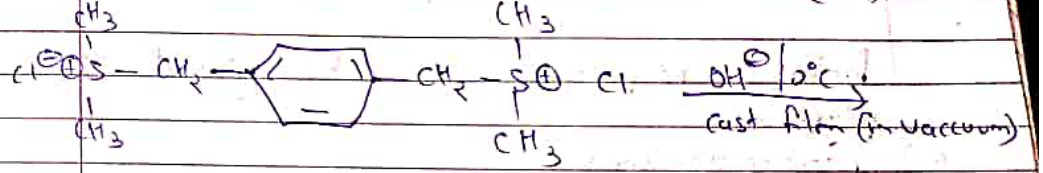
Indium tin oxide (it is act as anode)

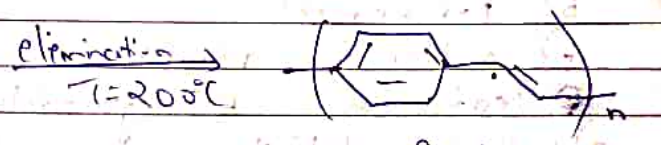
Glass / Plastic

b/w cathode & anode a electroluminescent polymer layer has been putted when current pass it emit light. The energy gap b/w these and conduction band में अंतर है $e^{\ominus}$ transfer होते & electricity flow and conductivity occurs. and light emits.

PPV preparation





Precursor  PPV

elimination
T=200°C

Uses & application

① PLED

4) Liquid crystalline polymers

Liquid crystalline polymers are those polymers that are capable of forming regions of highly ordered structure while in liquid phase.

It has high Mechanical Strength at high temperature.

High heat stability & flexibility

A very commonly known liquid crystalline polymer is Kevlar. It is an aromatic polyamide. It is prepared by the polycondensation of aromatic dichloride and aromatic diamines.

Uses

1) It is used in aerospace and aircraft industries
2) It is used in the fabrication of protective wears including bullet proof vests.

Biodegradable Polymers
(Same as starting wala)

factors Responsible for biodegradation of polymers:

a) Microorganisms
b) Environment
c) Nature of Polymer

Features of Biodegradable polymers

a) Biodegradability depend on functional group
eg → ester > ether > amide
3) Hydrophilic has more degradable than hydrophobic
3) Amorphous are more degradable than crystalline

classification

Natural Biopolymers	Biosynthesis Biopolymers	Synthetic Biopolymers
obtain from Plant & animal ex→ Cellulose	obtained from Microorganisms eg→ PHB, PHV	Produced synthetically

Application

1) Used as food Packaging
2) Used in agriculture

Example

1) PHB (Polyhydroxy butyrate) produced by fermentation of glucose by bacteria
2) PHV
3) PHBV