Engineering chemistry - I

unit - I water and its treatment

Introduction

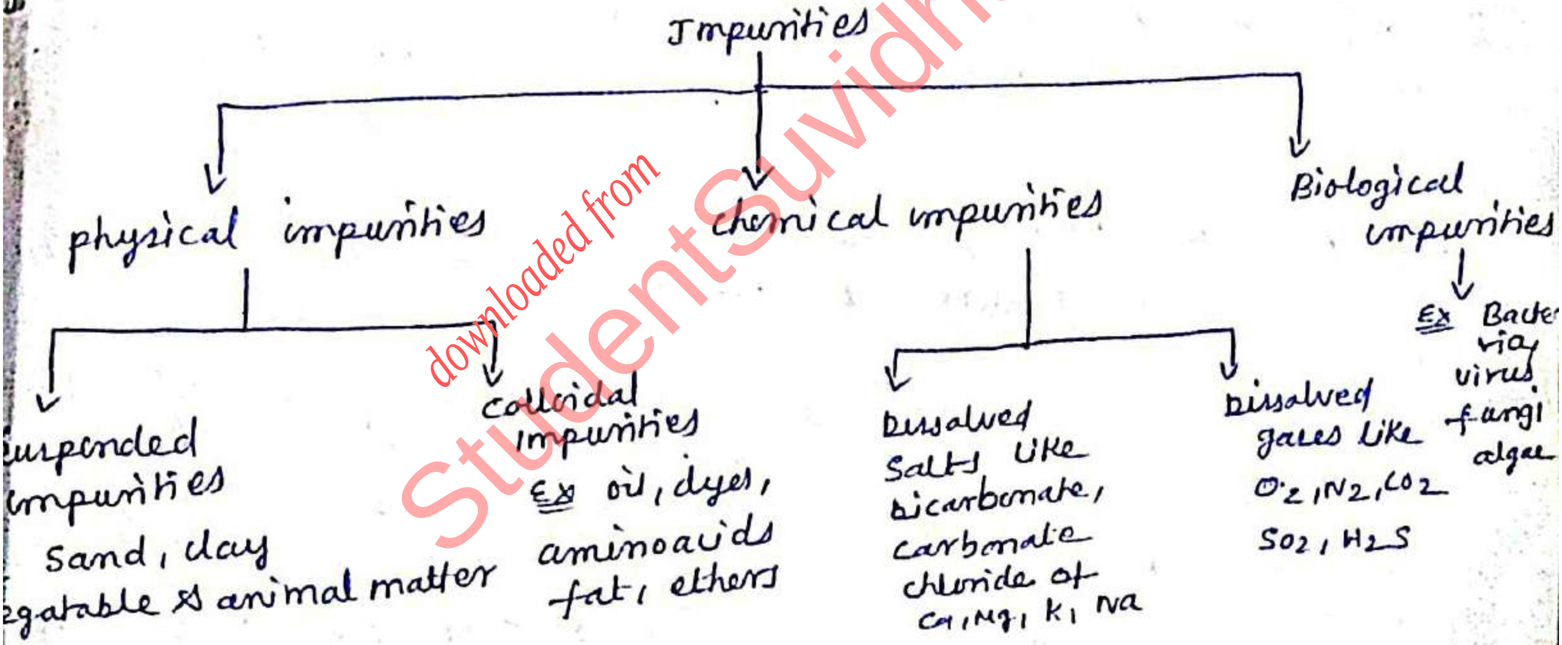
- Water is the most essential for all living beings on the earth.
- Hence without water, there is no life on the earth.

Sources of water

i) Natural water - Rain water
ii) Surface water - Rain water, river water, lake water & sea water
iii) underground water - spring water and, well water

Types of impurities

It can divided into three types



Hardness of water

The presence of dissolved salts like bicarbonates, chlorides and sulphates of calcium and Magnesium.

Types of water

1. Soft water
2. Hard water

Soft water :

i) It gives good lather with soap solution is calle
Soft water.

ii) The absence of dissalved salts of ca & Mg

Hard water :

i) It does not give good lather with soap soluti
is called as hard water.

ii) The presence of dissalved salts of ca & Mg

Difference between soft water & Hard water

Soft water	Hard water
1. It gives good lather with soap solution	It does not give good l with soap solution
2. Absence of dissalved salts of ca & Mg	presence of dissalved s of ca & Mg
3. It does not gives wine red colour with Erichrome black-T indicator.	It gives wine red colour with Erichrome black-T indicator.

Detection of hardness of water

It is detected by treating water with soap solu

$$\underset{\text{Soap}}{2C_{15}H_{31}COONa} + \underset{\text{Hard water}}{CaCl_2} \rightarrow (C_{15}H_{31}COO)_2Ca$$

Types of hardness

The types of dissalved salts present in wa
classified into two types.

1. Temporary hardness
2. permanent hardness

Temporary hardness

The presence of bicarbonates salt of ca & Mg called as Temporary hardness of water carbonate hardness of water (or) alkaline hardness of water.

Removed by

i) boiling the water

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2$$

ii) Adding Lime ($Ca(OH)_2$)

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaCO_3 \downarrow + CO_2 + H_2O$$

permanent hardness of water

The presence of chlorides and sulphates of Ca & Mg called as permanent hardness of water (or) non-carbonate hardness of water (or) non-alkaline hardness of H_2O

Removed by

i) Lime soda process → $CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2NaCl$

ii) Zeolite process (Na_2Ze)

$$MgSO_4 + Na_2Ze \longrightarrow MgZe \downarrow + Na_2SO_4$$

Total Hardness of water = Temporary Hardness + permanent hardness.

Differences between carbonate and non-carbonate hardness of H_2O

carbonate	non-carbonate
The presence of bicarbonates of Ca & Mg	The presence of chlorides and sulphates of Ca & Mg
It can be removed by boiling the water	It cannot be removed by boiling the water
Another name is alkaline hardness	Another name is non-alkaline hardness.

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Expression of hardness of equivalents of $CaCO_3$ standard

i) Molecular weight is 100 and equivalent weight is are whole number. Hence, the calculations in water simple and easy.

ii) $CaCO_3$ is the most insoluble salt that can be precipit during water treatment.

iii)
$$\text{The amount equivalent of } CaCO_3 = \frac{\text{Amount of hardness producing salt} \times \text{Molecular weight } CaCO_3}{\text{Molecular weight of hardness produ Sal}}$$

Hardness producing salt	Molecular weight
Mg^{2+}	24
$Mg(HCO_3)_2$	146
Ca^{2+}	40
$Ca(HCO_3)_2$	162
$MgCl_2$	95
$CaCl_2$	111

Units of hardness

i) **Parts per million (ppm)**

The number of parts of $CaCO_3$ equivalent hardn per 10^6 parts of water

ii) **Milligrams per Litre (mg/L)**

The number of milligrams of $CaCO_3$ equivalent hardness per litre of water

1 mg/L = 1 ppm

iii) **Clarkes degree (~~°Cl~~)(°Cl)**

The number of parts of $CaCO_3$ equivalent hardn per 70,000 parts of water

iv) Degree French (°Fr)

The number of parts of $CaCO_3$ equivalent hardness per 10^5 parts of water

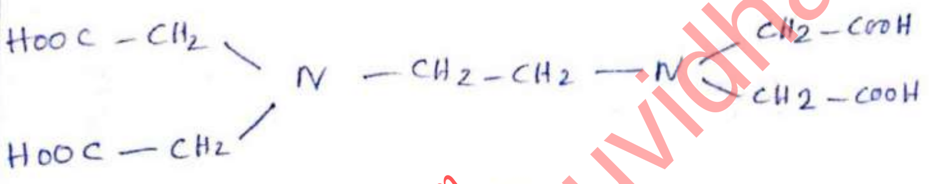
v) Milliequivalent per Litre (meq/L)

The number of milli equivalents of hardness present per litre.

Estimation of Hardness of water by EDTA method

- It is a complexometric method.
- It is more accurate, convenient and fast.
- It is widely used for the estimation of hardness of H_2O.

EDTA → Ethylene Diamine Tetra Acetic acid.



- EDTA is insoluble in water.
- Di sodium Salt (Na_2EDTA) is soluble in water.
- It is used as complexing agent.
- EDTA form stable complexes with Mg^{2+} & Ca^{2+} ions of hard water.

principle

$$M^{2+} + EBT \longrightarrow M^{2+}-EBT + EDTA \longrightarrow$$

(Ca^{2+}, Mg^{2+})

EBT ↓ Eriochrome black-T (Indicator) PH = 9-10 original colour (steel blue)

$M^{2+}-EBT$: unstable wine red complex
Indicator-metal ion complex

$[M^{2+} - EDTA] + EBT$
stable complex (steel blue)

* ~~wa~~ Buffer solution → Maintain constant pH value
↳ Ex : $NH_4Cl - NH_4OH$ mixture is added.

End point ⇒ wine red → steel blue (Indicator colour

preparation of solutions

i) standard hard water → 1g dry $CaCO_3$ + dil HCl + 1000 of H

ii) EDTA solution → 4g EDTA + 1000 ml of H_2O

iii) EBT indicator → 0.5 g EBT + 100 ml methanol

IV) Buffer solutions → 67.5 g NH_4Cl in 570 ml NH_4OH + 1000 ml of H_2O

procedure

i) Standardization of EDTA solution using standard hard water

Burette solution — EDTA
pipette solution — 50 ml of std. hard water
other solution — 10 ml Buffer solution
Indicator — Erichrome black - T
End point — wine red → steel blue colour

calculation

volume of EDTA = V_1 ml

1 ml of std. Hardwater = 1 mg of $CaCO_3$
50 ml of std. " = 50 mg of $CaCO_3$
50 ml of " " required V_1 ml of EDTA
V_1 ml of EDTA = 50 mg. of $CaCO_3$
1 ml of EDTA = $\frac{50}{V_1}$ mg of $CaCO_3$

i) Estimation of total hardness of water sample using Standardised EDTA solution

Burette solution — EDTA
pipette solution – 50 ml of sample water
other solution – 10 ml of Buffer solution
Indicator – Erichrome black-T
End point — Steel blue colour

Calculation.

Volume of EDTA = V_2 ml

50 ml of given sample water consumes = V_2 ml of EDTA

1 ml of EDTA = $V_2 \times \frac{50}{V_1}$ mg $CaCO_3$

∴ 1000 ml of given sample water = $V_2 \times \frac{50}{V_1} \times \frac{1000}{50}$

$= 1000 \frac{V_2}{V_1}$ mg $CaCO_3$

Total hardness $= 1000 \frac{V_2}{V_1}$ ppm

i) Estimation of permanent hardness of water sample using standardised EDTA solution

a) 100ml sample water in 250ml of Beaker
b) Boiled for temporary hardness cool and filter and make up into 100ml SMF.
c) Burette solution = EDTA
pipette solution = 50 ml Boiled sample water
other solution to be added = 10 ml of Buffer solution
Indicator = Erichrome black-T
End point = steel blue colour

calculation

Volume of EDTA = V_3 ml

50 ml of sample = V_3 ml of EDTA

$1\ ml\ of\ EDTA = V_3 \times \frac{50}{V_1}\ mg\ of\ CaCO_3$

$\therefore$ 1000 ml of given sample water consumes $y = V_3 \times \frac{50}{V_1} \times \frac{1000}{50}$

$= 1000 \frac{V_3}{V_1}\ mg\ of\ CaCO_3$

permanent hardness $= 1000 \frac{V_3}{V_1}\ mg\ of\ CaCO_3$

$= 1000 \frac{V_3}{V_1}\ ppm$

Temporary hardness $=$ Total hardness $-$ permanent hardness

$= 1000 \times \frac{V_2}{V_1} - 1000 \times \frac{V_3}{V_1}$

$= \frac{1000}{V_1} (V_2 - V_3)\ ppm$

—

Boiler feed water.

Definition

- The water fed into the boiler for the production of steam is called boiler feed water.

The water containing dissolved salts, gases and suspended impurities (physical & chemical) are used in boilers the following problems are

1) Scale and Sludge formation
2) boiler corrosion
3) Caustic embrittlement
4) priming and foaming

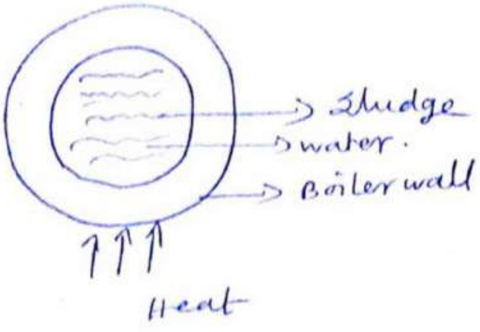
Boiler troubles (or Scale and Sludge formation

As water evaporate continuously in boilers for steam production, the salts precipitated on the inner walls of the boilers.

Sludge → If the precipitate formed is soft, and slimy it is called Sludge.

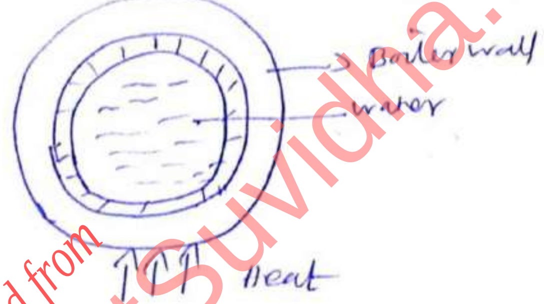
- It is formed by $MgCl_2$, $MgCO_3$, $MgSO_4$ & $CaCl_2$

- They have greater solubilities in hot water than cold water



Scale

1. → If the precipitate is hard and adhering on the inner walls it is called scale.
2. → Scales are formed by substances like $Ca(HCO_3)_2$, $CaSO_4$, & $Mg(OH)_2$



Removal of sludge (or) prevention of sludge

1. Sludges are poor conductors of heat
2. It formation can be prevented by using soft water
3. They can be removed by blow down operation method.

properties of scales

1. Scales are poor thermal conductors, Hence they act as partial heat insulators results wastage of fuels.

2. over heated and produce large amount of ste
and high pressure and explosion of boiler.

Removal of scales

1. Brittle scales may be removed by giving the
Shocks.
2. Loosely sticking scales can be removed by Scra
3. Firmly sticking scales can be removed by chem
reactions.

Comparision of sludge and scale

	Sludge	Scale
1.	It is a soft, loose & slimy precipitated	It is hard and adhe coating.
2.	It is formed by substances like $MgCl_2$, $MgCO_3$, $MgSO_4$, $CaCl_2$	It is formed by substa like $Ca(HCO_3)_2$, $CaSO$ $Mg(OH)_2$
3.	It is a poor conductor of heat	It is a thermal Insula
4.	Decrease the efficiency of boiler	Decrease the efficien of boiler and any Crac boiler explosion.
5.	It can be removed by scrapping off with a wire brush	It may be removed by giving thermal shocks, scrapping, chemical rea
6.	wastage of fuel is very large ⇄	wastage of fuel is comparatively less.
7.	Methods for removal of sludge I) blow down operation II) Scraping by wire brush	Methods for removal of scales. 1) Internal & exter treatmen

Softening or conditioning processes

Definition

Hard water is converted into soft water is called Softening (or) conditioning processes.

Types of process

1. Internal conditioning processes
2. External " "

External conditioning process

1. It is carried out before its entry into the boiler.
2. It is preventive method
3. High pressure boilers require this treatment.
4. It includes lime soda process, zeolite (permutit) process and ion exchange process.

Internal conditioning process

1. It is carried out in the boiler it self.
2. It is a corrective method.
3. ~~High~~ Low pressure boilers require this treatment.
4. It includes carbonate conditioning, colloidal conditioning, calgon conditioning, phosphate conditioning.

Difference between external & internal conditioning process of softening process.

(above the points 4 in External & internal conditioning write it)

Internal conditioning process

a) colloidal conditioning

1. In low pressure boilers, Scale formation can be avoided by adding organic substances (or colloidal substances like Kerosene, agar-agar, ta gelatin etc.

2. colloidal substances coated over the Scale form particles and convert into the loose ~~po~~ precipitate called sludge.

3. It can be removed by blow down operation.

b) phosphate conditioning :- 1. In high pressure

1. Scale formation can be avoided by adding sodium phosphate.

2. The phosphate reacts with Ca^{2+} and Mg^{2+} salts to give soft sludges of Ca & Mg phosphates

$$3CaSO_4 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2\downarrow + 3Na_2$$
$$3MgCl_2 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2\downarrow + 6Na$$

No	name of phosphate Salt	used in
1.	Trisodium phosphate (Na_3PO_4)	acidic wate
2.	Di Sodium hydrogen phosphate Na_2HPO_4	weakly acid water
3.	Sodium dihydrogen phosphate (NaH_2PO_4)	Alkaline w

c) calgon conditioning

1. calgon is sodium hexa meta phosphate

∴ $Na_2[Na_4(PO_3)_6]$

2. It reacts with Ca^{2+} to form highly soluble complex.

3. It prevents the precipitation of scale forming salt.

. calgon conditioning is betten than phosphate conditioning

$$2\,CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow$$
$$Na_2(Ca_2(PO_3)_6] + 2\,Na_2SO_4$$

) Sodium aluminate conditioning

1. Sodium aluminate reacts boiler water to give sodium hydroxide & gelatinous precipitate of coagulant aluminium hydroxide.

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3 \downarrow$$

2. Sodium hydroxide reacts with Mg^{2+} ions to give magnesium hydroxide

$$MgCl_2 + 2NaOH \rightarrow 2NaCl + Mg(OH)_2 \downarrow$$

3. Aluminium hydroxide & Magnesium hydroxide are produced inside the boiler.

4. Finely suspended & colloidal impurities, oil drops and silica formed.

5. It can be removed by pre-determined blow down operation.

External conditioning

Two methods

1. Demineralisation or ion-exchange process (o deionisation Proce
2. zeolite (or permutit process.

1. Demineralisation (or ion-exchange process (or) de ionisation process

Definition :

- Anions and cations are removed from the hard water is called de-ionisation process (or de mineralisation process.
- Soft water is not a demineralised water whereas demineralised water is a soft water.
- Demineralisation process, the ions present in water are ~~in~~ removed by ion exchangers.

process

cation exchangers (or cylinder - I

1. Hard water is passed through the I- cylinder absorbs all the cations like, Na^+, K^+, Mg^{2+}, Ca

called as cation exchangers

2. It is represented as RH_2 (or RH

3. Examples : Sulphonated coal
   Sulphonated polystryrene

4. commericially available are i) Amberlite IR-12
   ii) Dowox- 50

$RH_2 + CaCl_2 \rightarrow RCa + 2HCl$

$2RH + MgCl_2 \rightarrow RMg + 2HCl$

Ion-exchange (or) Demineralisation process

Definition

- Removal of all ions (cations and anions) rom the Hard water is called de-ionisation process (or) demineralisation process.
- Soft water is not a demineralised water whereas demineralised water is a soft water
- Demineralisation process, the ions present in water are removed by ion-exchangers.

Resins are classified into two types

1. cation exchange resin
2. Anion " "

ation (or) Acidic exchange Resin (RH^+)

- It is containing acidic functional groups ($-COOH$, $-SO_3H$, etc).
- It exchange acidic H^+ ions with other cations of hard water

xample Sulphonated (or) carboxylated polystyrene

rocess

- Hard water is passed through the cation resin. It removes all the cation like: Ca^{2+} & Mg^{2+}

$$2RH^+ + Ca^{2+} \longrightarrow R_2Ca^{2+} + 2H^+$$

nion or Basic exchange Resins ($R'OH^-$)

- It is containing basic functional groups ($-OH$, $-NH_2$ etc.)
- It exchange their OH^- ions with other anions of hard water

EX cross-linked polystyrene containing quaternary ammonium salts.

process

* It Removes all the anions like SO_4^{2-}, Cl^- etc.

$$R'OH^- + Cl^- \rightarrow R'Cl + OH^-$$

Finally

$$H^+ + OH^- \rightarrow H_2O$$

Regeneration

i) cation exchanger is regenerated by passing HCl (or) H_2SO_4 solution.

$$R_2Ca^{2+} + 2H^+ \rightarrow 2RH^+ + Ca^{2+}$$

ii) Anion exchanger is regenerated by passing dil. NaOH

$$R_2SO_4^{2-} + 2OH^- \rightarrow 2R'OH^- + SO_4^{2-}$$

Advantages

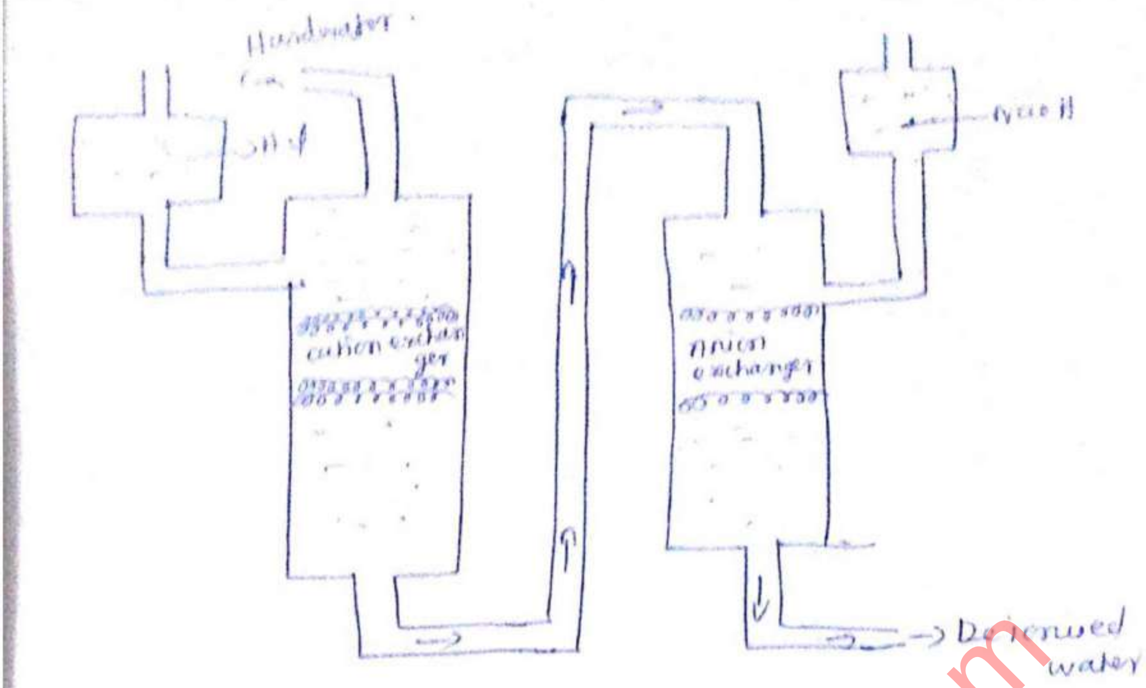
1 It is used to treat highly acidic (or) alkaline

2 It is used in high pressure boilers.

3. It produces water of very low hardness (up to 2 ppm)

Dis advantages

1. The equipment is costly.
2. Turbidity reduces the efficiency of the proce



Anion exchangers (on cylinder - II

1. It absorbs the anions like Cl^-, HCO_3, SO_4^{2-} called as anion exchangers.

2. It is represented as $R(OH)_2$ (or) ROH

3. Examples i) urea formaldehyde resin
   ii) Melamine Formaldehyde resin.

4. commercially available in i) Amberlite - 400
   ii) Dowex - 3

Completely free from anions and cations in the water are removed called as deionised water (or) demineralised water.

$$R(OH)_2 + CaCl_2 \longrightarrow RCa + OH^-$$

Regeneration

1. cylinder - I passed through the acid

$$RCa + HCl \longrightarrow RH + NaCl$$

2. cylinder – II passed through the base

$$RCl_2 + 2NaOH \longrightarrow 2NaCl + R(OH)_2$$

resin.

Advantages

1. It is used to treat highly acidic or alkalin water

2. It is used in high pressure boilers

Dis advantages

1. It is costly and more expensive method.

2. Turbidity reduces the efficiency of the proce

Zeolite (or) permutit process

Definition : The process of removing hardness producing salts from by using zeolites is called zeolite process

~~The zeolites are also known as permutit~~

* Zeolites are naturally occuring hydrated sod alumino silicate.

* general formula is $Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH$

$(x = 2-10,\ y = 2-6)$.

Types : Two Types

1. Natural zeolites : non-porous & greensand

Ex natralite : $Na_2O\ Al_2O_3 \cdot 4SiO_2 \cdot 2H_2$

2. Synthetic zeolites : porous & gel structure

* Synthetic form of zeolite is known as permutit.

* It is represented by Na_2Ze

process

- when hardwater is passed through a bed of Sodium zeolite (Na_2Ze), and exchange the sodium ions with Ca^{2+} & Mg^{2+} to form Ca & Mg zeolites.

$Mg(HCO_3)_2 + Na_2Ze \rightarrow MgZe + 2NaHCO_3$

$CaSO_4 + Na_2Ze \rightarrow CaZe + Na_2SO_4$

$MgCl_2 + Na_2Ze \rightarrow MgZe + 2NaCl$.

Regeneration

The exhausted zeolite is again regenerated by treating with 10% Solution of NaCl. (or) 10% brine solution.

$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$

$MgZe + 2NaCl \rightarrow Na_2Ze + MgCl_2$

Advantages

i) Hardness of water 1-2 PPM by this process water obtained.

ii) It can be used again

iii) No sludge is formed

iv) It occupies a small space.

v) It operates easily.

Dis advantages

i) Blocks the pores of the zeolite bed - Turbid water

ii) Decomposes the structure of zeolite - Acidic water

III) It produced resulting in boiler corrosion and caustic embrittlement.

IV) Regeneration is very difficult.

v) This process cannot be used for softening brackish water.

VI) Turbid water & highly acidic water cannot be treated.

Differences between zeolite and Demineralisation pr

	Zeolite process	Demineralisation pr
1.	It exchange only cations	It exchange cations & anions
2.	Acidic water cannot be treated.	Acidic water alkaline H_2O can be treated.
3.	It produces priming & foaming	No priming & foaming
6.	Suitable for all types of boilers	not suitable for high pressure boilers.
4.	It can be used in high pressure boilers.	It cannot be used in boilers.
5.	Hardness range 10-15 ppm	0-2 ppm.
7.	It occupies less space	more space

Portable water Treatment

Definition

Water that is used for drinking purpose known as potable water.

Standards of drinking water

Water used for drinking should be

1. colourless and odourless
2. Free from any suspended or colloidal impurities
3. Free from micro organisms and bacteria

untreated water contain pathogens, chemical pollutants and other component like odour, turbidity, algae etc.

Treatment method

i) Heating (or) boiling

a) Heat kills disease causing micro organism.

b) Boiling does not leave any residual protection.

) Filtration

Potable pump filters remove most bacteria & protozoa, But they do not kill viruses.

) Activated charcoal adsorption

a) It can remove chlorine from treated water.

b) It protects water against pathogens.

) chemical disinfection

a) chemical disinfection with Cl_2 & I_2 results from oxidation of cellular structures and enzymes.

b) Sodium dichloroisocyanurate (NaDCC) is used for water treatment.

c) Iodine kills many common pathogens in fresh water sources.

d) ozone finds use in municipal water treatment plants, food processing units and healthcare organisations.

v) ultra violet purification

In solar water disinfections (SODIS), microbs are destroyed by temperature and uv radiation provided by the sun.

vi) Solar distillation

These methods are commonly used at household level in developing countries, by recreational enthusisasts, millitary personnel Survivalists.

Desalination of Brackish water

Definition

- The process of removing common salt (Nacl) from the water is known as desalination
- Water containing high concentration of dissolved salts is known as brackish water

Water quality based on dissolved salts as

1. Freshwater – contains < 1000 PPM of dissolved
2. Brackish water – " 1000 – 35000 PPM "
3. Sea water – " >35000 PPM "

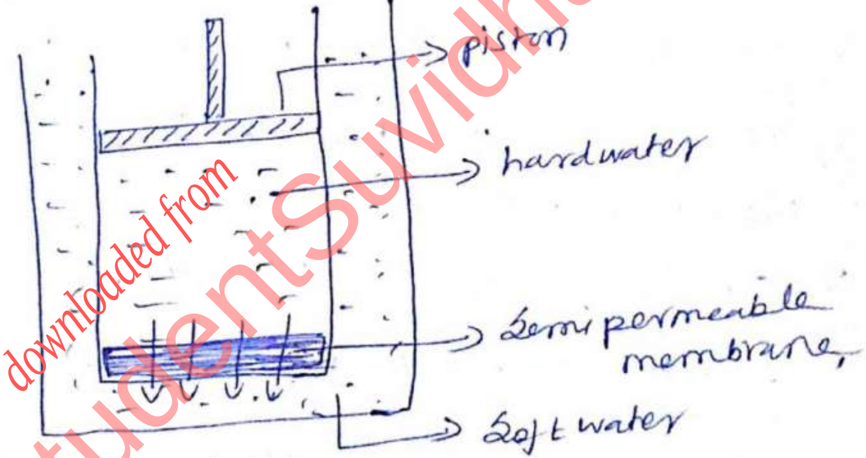
Some techniques are used for desalination of sea water & brackish water

i) Distillation
ii) eletrodialysis
iii) reverse osmosis
iv) Distillation
v) Freezing

Reverse osmosis process

principle :- osmosis

- When two solutions are separated by a semi-permeable membrane, the solvent molecules will move from dilute solution to the concentratrated solution.
- This process is known as osmosis.
- when a hydrostatic pressure applied on the concentrated side, solvent molecules move from concentrated solution to the dilute solution.
- This process is known as Reverse osmosis



process

- In this method, hard water is taken in the inner vessel.
- Soft water is taken in the outer vessel.
- Hard & soft water are separated by semipermeable membrane.

- A hydrostatic pressure applied on the har water side.
- The solvent molecules move from concentrated solution to dilute solution.
- Thus softening of hard water takes place.
- Sulphone, cellulose acetate, polyamide and poly acryle nitrile are used as semi-permeable membranes.

Advantages

- This process is used for purify the sea wate for drinking purpose.
- The life time of the membrane is high.
- It removes all types of impurities (ionic, non-ionic, colloidal)
- This process is used for high pressure boilers
- Membrane can be replaced with in short tim
- It is very less expansive method.

Up Flow ~~An~~ Anaerobic Sludge Blanket (UASB) process

principle

- In this process waste water enters the reactor from the bottom & flows upward.
- A suspended sludge blanket are filtered.
- It is used for waste water treatment

process

- UASB is a single tank process.
- It uses a reactor.
- Reactor are constructed using concrete (or) other water tight material.
- It can be designed in a circular (or) rectangular.
- waste water is pumped from the bottom into the reactor.
- Bacteria growth on the sludge.
- A sludge blanket is comprised of microbial granuals of 1 to 3 mm in diameter.
- The microorganisms in the sludge layer degrade organic compounds
- Gases like methane, CO_2, biogas are released.
- The rising bubbles mix the sludge.
- equilibrium forms a stable and suspended sludge blanket
- The effluent is extracted from the top of the tank.
- A gas - liquid - solid separator (GLSS) separates the gas from the treated waste water and the sludge

Advantages

- Biogas are produced & used as energy source.
- Sugars dissolved in the liquid waste stream converted into gas quickly.

- High reduction in organics.
- The nutrient rich effluent used as soil fertiliser after composing.

Disadvantages

- Long start up time.
- constant source of electricity is required.
- Difficult to maintain proper hydraulic Condit
- Requires expert design and construction Super
- Dilute waste water streams with 3%. total suspended solids (TSS) with particle s < 0.75 mm

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Boiler troubles ~~(or~~ Boiler feed water (or) Disadvan of using hardwater in boilers

Definition

- water used in boilers to generate steam known as Boiler feed water.
- Hard water is used in boilers many troub will arise. They are

1. Scale & Sludge formation
2. corrosion of the boiler metal
3. caustic embrittlement
4. Foaming & priming

1. Boiler Scale formation

On heating continuously, the dissolved salts in hard water gets deposited as a coating on the boiler surface. This is known as boiler scale.

Disadvantages of Boiler scale

i) Boiler scale is a bad conductor of heat, so the wastage of fuel.

ii) The scales block the safety valves, the boiler explosion.

iii) corrodes the boiler metal

iv) Boiler metal loses its strength

v) corrosion of boiler metal

It is due to the presence of

a) Dissolved oxygen

b) Dissolved carbon dioxide

c) dissolved salts.

d) chemical

e) Electrochemical

f) environment

g) mineral acids

h

a) Dissolved oxygen → It attacks the boiler metal at high temperature.

$$4Fe + 6H_2O + 3O_2 \longrightarrow 4Fe(OH)_3 \downarrow$$

b) Remedies

Dissolved oxygen can be removed by chemical or mechanical methods by deaeration.

b) Dissolved CO_2 → It produces carbonic acid which corrodes the metal.

Remedies

- By removing CO_2 using lime
- Removed by mechanical deaeration method

Mineral acids → It attacks the boiler metal and corrode it.

Remedies

By neutralising mineral acids with bases like soda ash.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

caustic embrittlement (intercrystalline crack

Definition

- corrosion which occurs at the cracks and ri inside the boiler parts is called caustic embrittle
- This effect is due to the presence of sodium hydroxide in water.
- This problem can be avoided by using lime.

$$Fe + 2NaOH \rightarrow Na_2FeO_2 + H_2\uparrow$$

prevention

It can prevented by

i) using sodium phosphate & sodium carbonate

ii) by adding tannin, lignin to the boiler water

priming & Foaming (carry over)

priming

Definition

- It is the process of production of wet steam
- It is the rapid and violent boiling of H_2O

It is caused by

a) High steam velocity

b) very high water level in the boiler

c) Sudden boiling of water

d) very poor design of the boiler

prevention

It can be controlled by

a) control the velocity of steam

b) Keep the water level lower.

c) Good boiler design proper and uniform heating

d) using treated water

Foaming

Definition

* The formation of stable bubbles above the surface of water is called foaming.

* It is caused by

a) presence of oil & grease

b) presence of finely divided particles.

prevention

It can be prevented by

a) adding coagulants like sodium aluminate aluminium hydroxide.

b) adding anti-foaming agents like synthetic polyamides.

2mark Questions (Additional questions)

What are the methods used to prevent Scale formation?.

- Scraping n wire brush used.
- blow down operation.
- thermal shocks.
- adding chemicals

What are boiler compounds. Give two examples

Scale forming substances can be removed by adding chemicals directly to the boiler.

Ex Na_2CO_3, Na_3PO_4

3. What are the methods used to soften hardwater

i) External treatment – zeolite process, ion-exchange, Reverse osmosis

ii) Internal " – carbonate, colloidal, phosphate, Sodium aluminate, calgen.

Mention the units used for expressing hardness of water?

i) PPM ii) Mg/L iii) clarks degree iv) French degree

What are ion exchange resins?

Ion-exchange resins are insoluble, long chain, cross-linked organic polymers which are permeable due to their micro porous structure

Name the salts responsible for Scale and Sludge.

Scale : $Ca(HCO_3)_2$, $CaSO_4$

Sludge : $MgCO_3$, $MgCl_2$

7. What is blow-down operation?

It is process of removing a portion of concentrated water by freshwater frequently from the boiler durring steam production.

Treatment method

Treatment	used in
Heating	Destroy the micro organism
Filtration	Remove bacteria & protozoa.
Activated charcoal adsorption	prore. Destroy the pathogen
chemical disinfection	purify the water treatment
a) Sodium dichloro isocyanurate	Kills the pathogen (on destroy
b) Iodine	municipal water treatment
c) ozone	food processing units
ultraviolet purification.	destroyed the microbes
Solar distillation	purify the water

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FUELS

A source of heat energy is called a fuel. The term fuel is applied to a combustible substance which on burning in presence of O_2 produces a large amount of heat that can be used economically for domestic and industrial purposes.
During the combustion of fuels new bonds are formed and old bonds get breaked involving a chemical rxn ∴ fuels are also reffered as chemical fuels.
Other than combustion, Nuclear fuels also liberate energy by fission or fussion of nuclei. (Nuclear fuel Energy > chemical fuel)

* fossile fuels are regarded as Stored Solar energy.

Solar Energy ⟶ vegetation ⟶ Cellulose (not used by Plants)

$(H_2O + CO_2 \xrightarrow[\text{chlorophyll}]{h\nu}$ Carbohydrate) used by plants

(Photosynthesis)

Cellulose ↓ fossilization ⟶ Peat ⟶ Coals ⟶ chemical energy

Classification of fuels

1. Occurance.

Primary

Occurs in nature & can be used directly or after little Processing
e.g. wood, Peat, Coal, Petroleum & natural gas

Secondary

Derived from Primary fuels by chemical Processing.
e.g. Coke, charcol, Kerosene, Coal gas, Producer gas.

2. Physical State

Primary

- → Solid fuels
  - wood
  - Peat
  - lignite
- → Liquid
  - Crude oil
- → gaseous
  - Natural gas

Secondary

- → Solid fuel
  - Coke
  - Charcol
- → Liquid
  - Petrol, LPG
- → Gaseous
  - Coal gas
  - water gas

Calorific value of fuel (Judges the eficiency of fuels

Calorific value is defined as the total quantity of heat liberated when a unit mass of a fuel is burnt Completely.

Unit of Calorific value

CGS Cal/gm (Solid/Liquid) Cal/cm^3 (gases)

1 k Cal = 1000 cal
1 k Cal = 3.968 B.Th.U (British thermal unit)
1 K Cal = 2.2 CHU (Centigrade heat unit)

☆ GROSS CALORIFIC VALUE

It is the total amount of heat generated when a unit quantity of fuel is completly burnt in oxygen and the products of combustion are cooled down to the room temp. (15°C or 60°F)

* fuel contains Hydrogen $\xrightarrow{\text{Combustion}}$ H_2 converted into steam ⏋ cooled down
This added in CV ⟵ latent heat evolved. ⟵ H_2 converted into H_2O ⟵

↳ therefore GCV also called higher calorific value (HCV)

☆ NET CALORIFIC VALUE

It is defined as the net heat produced when a unit quantity of ~~heat~~ fuel is completly burnt and the product of combustion are allowed to escape.

* water vapour are escape with hot combustion gases. ∴ less CV is available

LCV = HCV − latent heat of water vapour

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O$$
$$2g \qquad 16g \qquad 18g$$

H g hydrogen ⟶ 9H g of H_2O
1g H_2O ⟶ 587 Cal/g latent heat of water vapour
9H g H_2O ⟶ 9*H*587 (L.H)

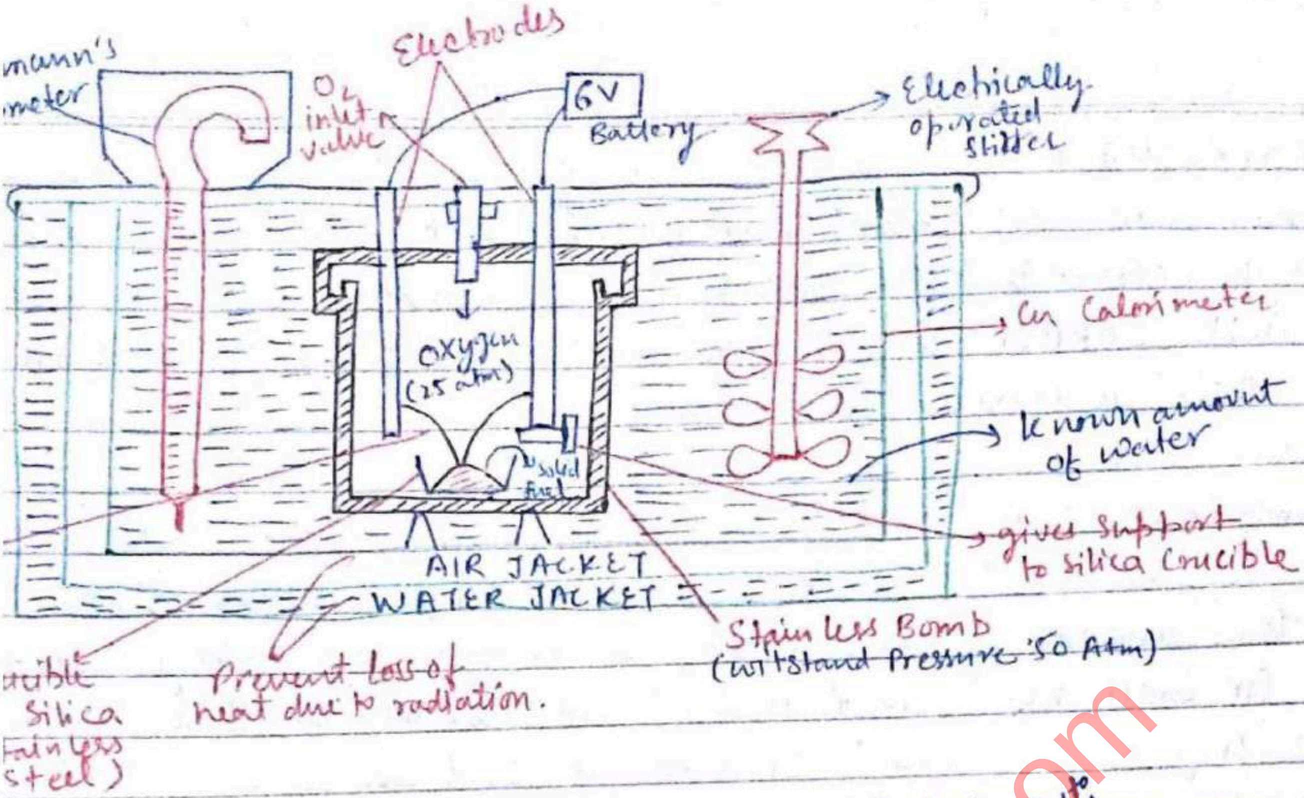
∴ LCV = HCV − 9*H*587

(if % of H in fuel is given, LCV = HCV − 0.09*H*587)

Determination of Calorific value of Solid & Non-volatile liquid

BOMB CALORIMETER

Principle: A known amount of the fuel is burnt in excess of oxygen and the heat liberated is transferred to a known amount of water. The CV is determined by using Principle of Calorimetery i.e. Heat gained = Heat lose



taken (g or 1g) → Initial temp of water was noted → fuel started to burn → heat transfered to H_2O → max temp is noted (of H_2O) → time taken to cool the H_2O also noted.

wgt of fuel sample $= x\,g$
wgt of water in Calorimeter $= W\,g$
~~wgt~~ equivalent of Calorimeter, Stirrer, bomb, thermometer $= w\,g$
Initial temp. of water $= t_1\,°C$
final temp. of water $= t_2\,°C$
HCV $= C$ cal/g
Heat gain by water $= W(t_2 - t_1) \times$ specific heat of water $(=1)$ cal
Heat gain by Calorimeter $= w(t_2 - t_1)$ cal
Heat liberated by fuel $= xC$ cal

$$\text{Heat gain} = \text{Heat loss}$$

$$\therefore \quad xC = (w+W)(t_2 - t_1)$$

$$C = \frac{(w+W)(t_2 - t_1)}{x} \text{ Cal/g} \quad \text{—①}$$

$$NCV = C - 0.09 \times H \times 587 \text{ Cal/g} \quad \text{—②}$$

Water equivalent: no. of Calories required to heat Calorimeter by 1°C

$$w = MS$$
S → specific heat
Mass (Calorimeter)

Also, $w = M_1S_1 + M_2S_2 - - -$

⇒ Correction

1. fuse wire correction: During ignition Mg wire produced heat. & is included in GCV, that has to be removed.
2. ACID CORRECTION: During Combustion. S & N are oxidised to their acids under high Pressure & temp.

$S + O_2 \longrightarrow SO_2$

exothermic $\left\{ \begin{array}{ll} 2SO_2 + O_2 + 2H_2O \longrightarrow 2H_2SO_4 & \Delta H = -144,000 \text{ cal} \\ 2N_2 + 5O_2 + 2H_2O \longrightarrow 4HNO_3 & \Delta H = -57160 \text{ cal.} \end{array} \right.$

the amount of H_2SO_4 & HNO_3 is analysed by washing Calorimeter

→ for each ml of N/10 H_2SO_4 formed, 3.6 cal should be substracted.

→ 1mg of S formed's correction is 2.25 cal.

→ for each ml of N/10 HNO_3 formed, 1.43 cal must be substracted.

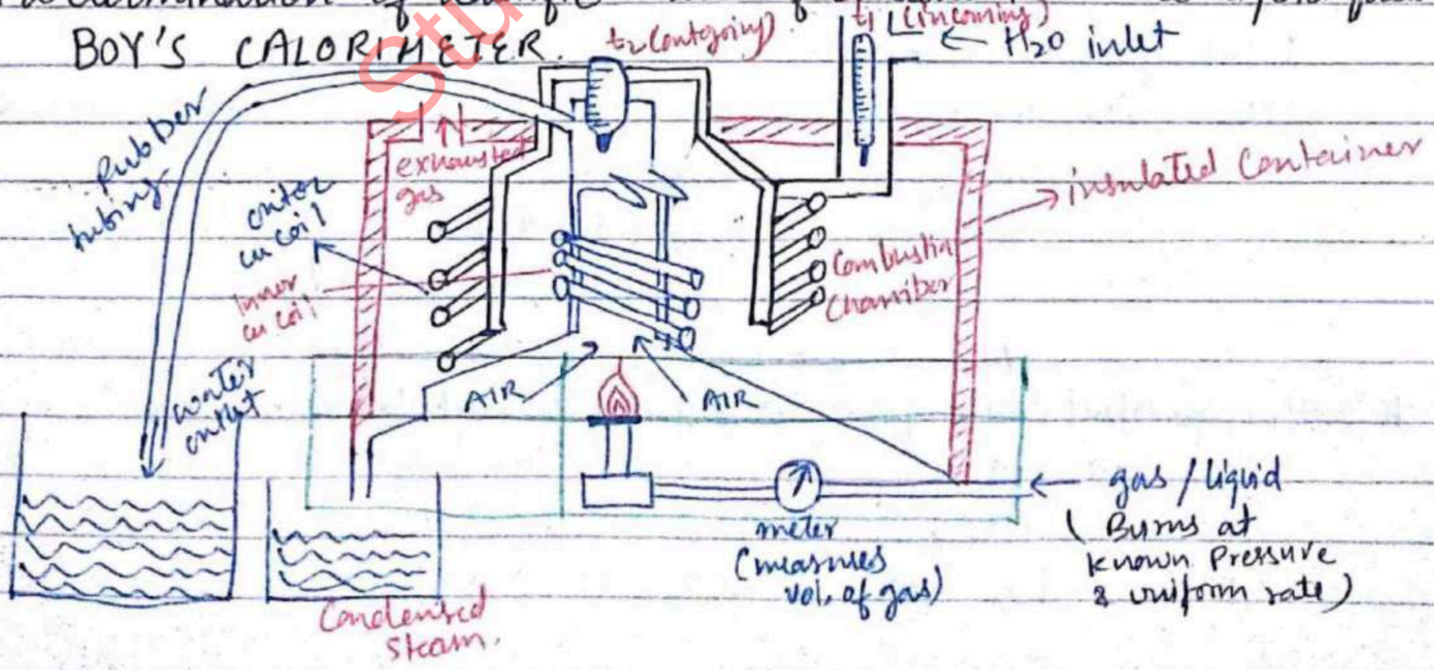
3. Cooling Correction. Due to simultaneous cooling & heating. there is heat loss due to radiation & hence highest temp is slightly less than that obtained. if no heat is lost.

if time taken to cool down the known water is x & rate of cooling is dt, then C.C = xdt.

$$\therefore \quad GCV = \frac{(W+w)(t_2 - t_1 + CC) - [f.w.c + A.C)}{\text{Mass of fuel.}}$$

Determination of calorific value of Gaseous & volatile liquid fuel.

BOY'S CALORIMETER.



→ 15 min Process of fuel Burning & water circulation.

→ Heat Produced by Burning is transferred to water in Cu coil. & steam gets condensed.

→ Noted
- vol. of gas burnt. in t time (converted to STP. ($V\,m^3$)
- wgt of H_2O passed in t. time. (W kg)
- temp of incoming & outgoing water (T_i & T_o)
- wgt of H_2O condensed. (m)

☆ Rise in temp = $T_o - T_i$, $GCV = C$

heat absorbed by circulating water $= W(T_o - T_i)$

heat Produced by Combustion of fuel $= VC$

heat gain = heat loss

$$\therefore \quad C = \frac{W(T_o - T_i)}{V} \quad — ①$$

wgt of water condensed per m^3 of gas $= m/v$ kg.

$\therefore$ latent heat of steam per m^3 of gas $= \frac{m}{v} \times 587$ kCal

$$NCV = GCV - \frac{m}{v} \times 589 \text{ kCal}/m^3.$$

Theoretical calculations of C.V. of fuel.

Acc. to Dulong, CV of fuel is the sum of CV of its constituents. CVs of C, H & S are 8080, 34500 & 2240 kCal/kg. resp.

if O_2 is there, $\therefore O_2 + 2H_2 \rightarrow 2H_2O$ and H is not available for combustion called fixed Hydrogen.

H available for combustion = Total mass of H − fixed Hydrogen.

8g of $O_2 \longrightarrow 1g\ H_2$

1g of $O_2 \longrightarrow \frac{1}{8}g\ H_2$ (fixed H)

$\therefore$ H available $=$ Total H $- \frac{O}{8}$

Dulong formula

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

$$NCV = GCV - 0.09H \times 587 \text{ kCal/kg}$$

* characteristics of good fuels.

① Suitability
② High CV (↑ heat/ unit mass or volume better is the fuel)
③ Ignition Temperature (lowest temp to which fuel must be heated so that it starts burning smoothly)
- Best fuel should have moderate Ignition temp.

④ Moisture Content (low moisture high CV)
⑤ Non-Combustible matter (clinkers) → reduces heating value & involves cost of the disposal.
⑥ Velocity of combustion must be moderate.
⑦ Products of combustion should not be harmful.
⑧ fuel should be available in large amount at low cost.
⑨ low smoke formation.
⑩ A combustion should be easily started or stop.

WOOD

freshly cutted.
↑ moisture content (25 to 50%)
↓ CV

Air-Dried.
↓ moisture content (10 to 15%)
Burns with long non-smoky flame.

* In air dried wood although ash content is low, the O_2 is very high. This makes its CV less. Still its low Ignition temp., non-Smoky flame & absence of ash make it best.

wood charcoal → destructive distillation of wood.
↳ Produce activating carbon → decolourisation in sugar industries.

COAL (fossil fuel) — Coalification —

WOOD → PEAT → Brown Coal → Bituminous Coal → Anthracite
$2(C_6H_{10}O_5)_n$ (Spongy) (High T & P lose moisture & Volatile matter) (Brittle Coal) (Metamorphism)

Carbon Content →
H_2 & N_2 & O_2 Content ←
Volatile matter & moisture ←
CV (Cal/g) →

☆ Analysis of Coal

1. Proximate Analysis : The obtained data varies with the procedure adopted and hence it is called Proximate analysis. Gives info. about Practical utility of coal.

A) Moisture Content wet coal → Exposed to atmosphere → dried Coal → heat at 105-110°C in electric hot air oven for 1 hour ⟶ Cooled in dessicator & weigh

$$\% \text{ of Moisture Content} = \frac{\text{loss in weight of Coal}}{\text{weight of Coal taken}} \times 100$$

B) Volatile Matter (Combustible gases like H_2, CO, CH_4 & C_2H_6)
Coal from Step A ⟶ heated in a Pt Covered Crucible at 950 ± 20°C for 7 min ⟶ Crucible is Cooled in air, then in dessicator ⟶ . weighed.

$$\% \text{ of V.M} = \frac{\text{loss of weight of Coal}}{\text{weight of Coal taken}} \times 100$$

C) Ash (Silica, magnesia, lime, alumina, iron oxide etc.)
Coal from Step B ⟶ heat at 700 ± 50°C for ½ hour without Covering ⟶ Cool & weigh.

$$\% \text{ of Ash} = \frac{\text{weight of residue}}{\text{weight of Coal taken}} \times 100$$

Ash → Intrinsic (oxide of Na, K, Mg, Ca, Si)
(mineral matter originally Present in Vegetable matter from which Coal formed. This can't be removed.)
Ash → Extrinsic (clay, $CaSO_4$, $CaCO_3$, Fe_2O_3)
(clay, gypsum, dirt which gets mixed up during mining & handling coal)

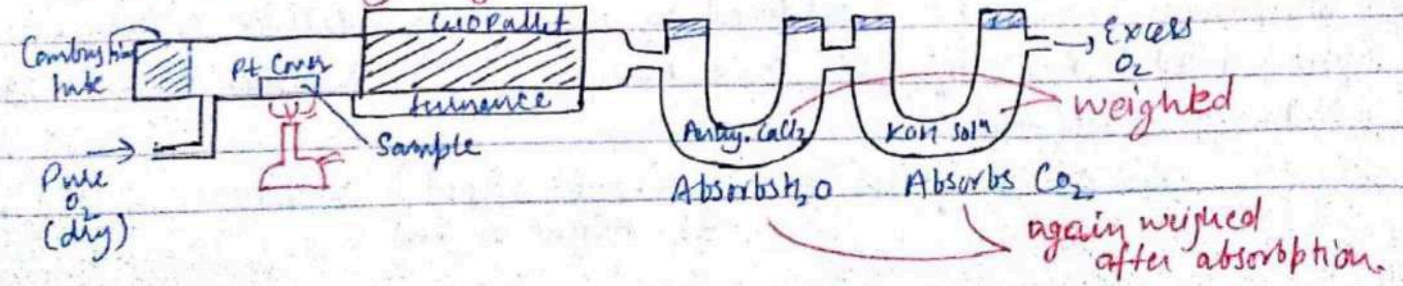
D) fixed Carbon This represents the quantity of Carbon that Can be burnt

$$\% \text{ of fixed Carbon} = 100 - [\% \text{ of Moisture} + \% \text{ of V.M} + \% \text{ of ash}]$$

☆ The term is misnomer because it Contains other non-volatile elements

2. Ultimate Analysis It is necessary to classify Coal by determine the % of various Components to fix its Cost & to know its uses.

A) Carbon & Hydrogen



$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$

$CaCl_2 + 7H_2O \longrightarrow CaCl_2 \cdot 7H_2O$

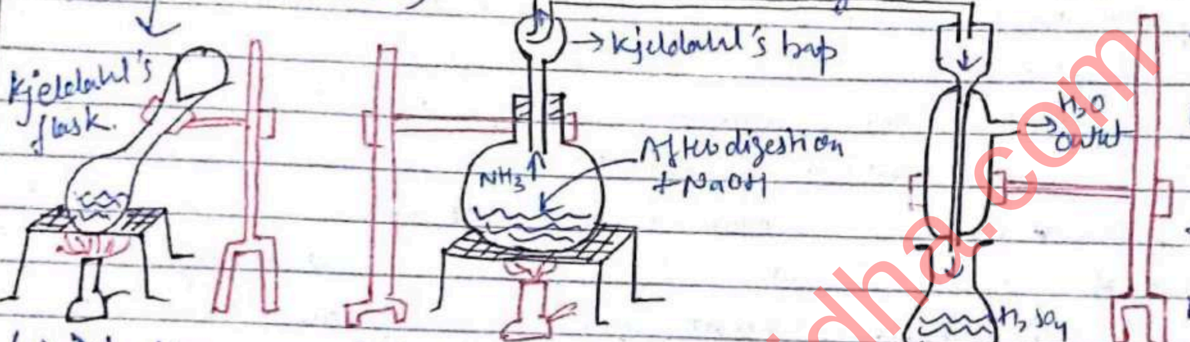
weight of sample (x), Inc. in wgt of $CaCl_2$ (y), ↑ in wgt of KOH (z)

$\% \text{ of carbon} = \frac{12}{44} \times \cancel{y} z \times \frac{1}{x} \times 100$

$\% \text{ of Hydrogen} = \frac{2}{18} \times y \times \frac{1}{x} \times 100$

B.) Nitrogen

$\underset{\text{(from coal)}}{\text{Nitrogen}} + H_2SO_4(\text{Conc.}) \xrightarrow[\text{Catalyst}]{K_2SO_4 + HgSO_4} (NH_4)_2SO_4$



(a) Digestion (b) Kjeldahl's distillation.

★ NH_3 gas liberated in known vol. of a standard sol^n of acid.

★ The not used acid is determined by titrating with NaOH

$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$

$NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

weight taken coal (W), vol. of acid used (V_1), Normality of acid (N_1)

V_1 ml of N_1 acid $= V_2$ ml of N_2 NH_3

V_2 ml of 1 normal NH_3 sol^n $= V_1 N_1$

$\therefore V_2 = V_1 N_1$

$\boxed{\begin{array}{l} 1000\text{ ml of } 1N \\ NH_3\ sol^n \equiv 17g \\ NH_3 = 14g\ N \end{array}}$

$\therefore \%\ V_2 \text{ ml of } 1N\ NH_3\ sol^n = \frac{14}{1000} \times V_1 N_1 \times \frac{1}{W} \times 100$

$\% \text{ of Nitrogen} = 1.4\ V_1 N_1 / W$

3.) Sulphur S in Coal ⟶ oxidised by fuming HNO_3 into H_2SO_4 ⟶ H_2SO_4 precipitated to $BaSO_4$ by $BaCl_2$ ⟶ $BaSO_4$ is filtered & heated to constant Vol. ⟶ $BaSO_4$ is weighed.

$\% \text{ of Sulphur} = \frac{32}{233} \frac{(\text{weight of ppt})}{\text{weight of coal}} \times 100$

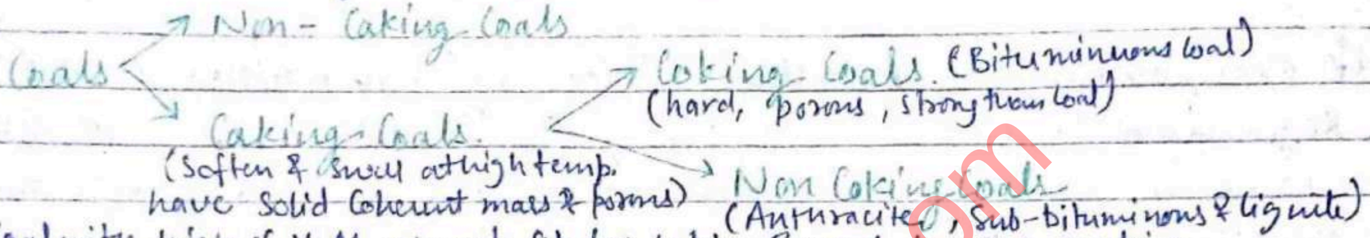
* V.M - Volatile Matter

D) Ash ⟶ Same as in Proximate analysis

E) Oxygen % of $O_2 = 100 - [\% H_2 + \% C + \% N + \% S + \% ash]$

* Carbonization of coal. (Coal ⟶ Coke)

Heating of coal in absence of air at high temp. and the decomposition of coal yields a residue rich in carbon content. This coke is lustrous, dense porous and strong with coherent mass.



* Coal with high % V.M. are not fit for coking & used for gas making.

PROCESS: Moisture & occluded gases are driven off.

↳ at 260°-270° C, H_2O, H_2S, some low alkenes & alkanes are evolved.

↳ at 350°C Decomposition of coal. → at 400°C caking coal become soft & plastic → 700°C H_2 is evolved. → 800°C main gases evolved → foamlike appearance → further temp. Coke is obtained.

Characteristic	Low temp. Carbonization	High temp. Carbonization
Temp.	500-700°C	1000-12[illegible]
Yield	75-80%	65-75%
V.M.	5-15%	1-3%
Mechanical strength	Not strong	Strong.
Hardness	Soft coke	Hard coke
use	Domestic use	Metallurgical use.
Yield of gas	low	high
C.V. of gas	higher	lower
tar & gas (C_nH_y)	higher	lower
% of aromatics	lower	higher
Smoke produced	Smokeless	Smoky

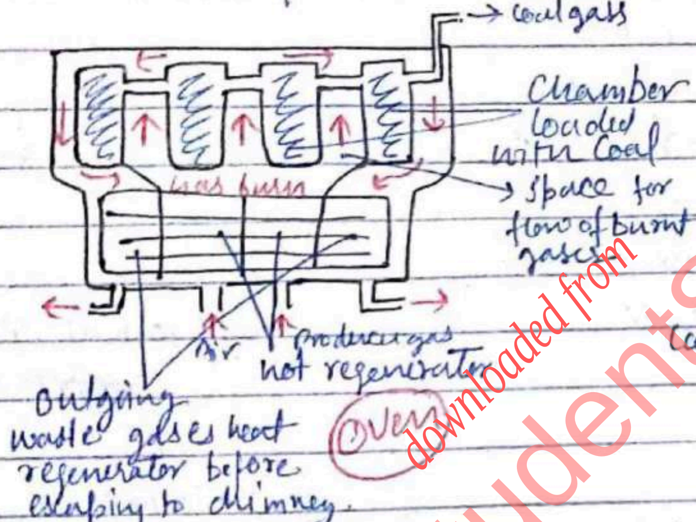
Metallurgical coke.

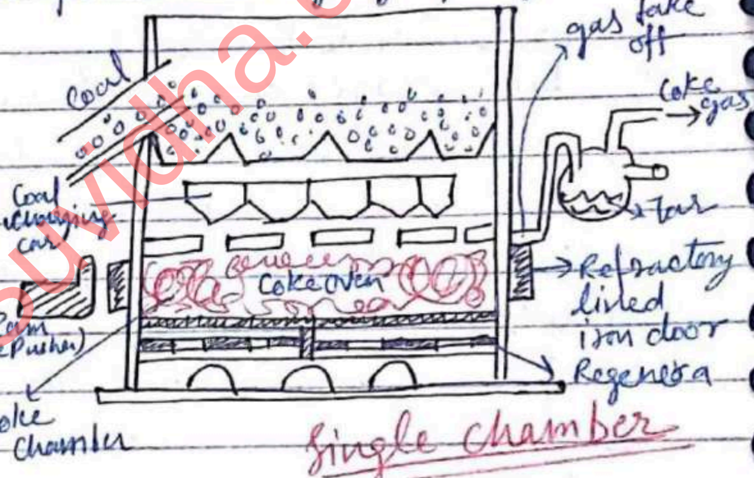
PROPERTIES

- Reactivity (ability to react with CO_2, O_2 & steam, air) should not be too high
- C.V. (should be high)
- Combustibility (easy burning) (weak coke > strong coke)
- Size (should be medium if low → cause choking if large → Non-uniform heating)
- Strength (to widthstand the weight of ore, flux etc.)
- Porosity (to provide contact b/w O_2 & C for complete combustion)
- Cost (cheap & easily available)
- Purity (moisture ↓ C.V & ash hinders heating and reduce rate of combustion.)

⇨ Manufacturing of Metallurgical Coke By "OTTO HOFFMANN OVEN"

Regenerative Principle of heat economy: Utilization of the waste fuel gases for the heating of the checker work of bricks. Moreover all the valuable products are recovered from the outgoing flue gases.





Single chamber

The ottohoffmann oven consists of number of narrow rectangular (12 × 4 × 0.5 m or 14 × 5 × 0.5 m) ~~bricks.~~ Chambers made up of silica bricks.

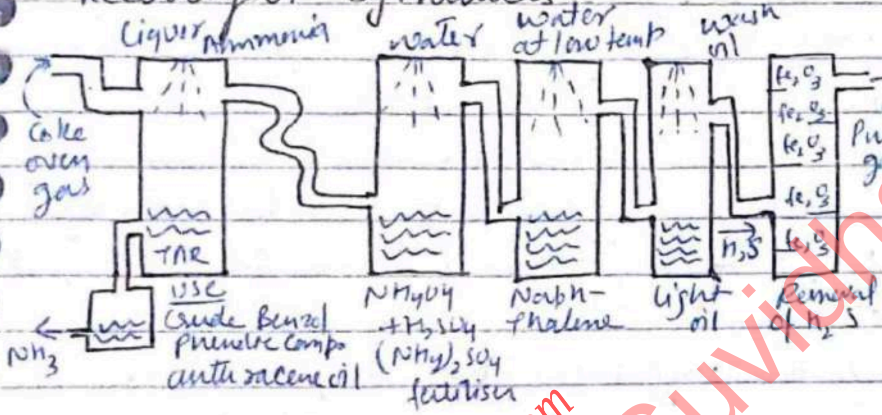
→ so tightly closed no air can enter

→ Coke oven are heated to 1200°C by burning gaseous fuels. → Coal adjacent to oven walls gets heated, a plastic zone is formed which moves towards the centre. Vol. of coal ↓ due to removal of V.M in the form of tar & gases at 500°C. Now, the plastic mass solidified into hard & porous mass called Coke. hardness is due to dehydrogenation accompanied by aromatization of coal. The process take 11 to 18 hours. & red hot coke is pushed out by Ram. which is electrically driven (Yield = 75%)

? The Quenching of red hot coke is achieved by Spraying water (wet Quenching) or by passing inert gases from boilers (dry quenching) why Dry quench is advantageous over wet quench ?

Because the coke produce is more strong & dense. Moreover in wet quenching the sensible heat of the coke is wasted whereas in dry quenching the inert gases after quench become heated up & are then circulated to boilers where they pre-heated the boiler-feed water and then recirculated for cooling fresh charge of coke.

Recovery of By Products



★ wash oil with benzene homologues is called Light oil.

$$fe_2O_3 + 3H_2S \rightarrow fe_2S_3$$

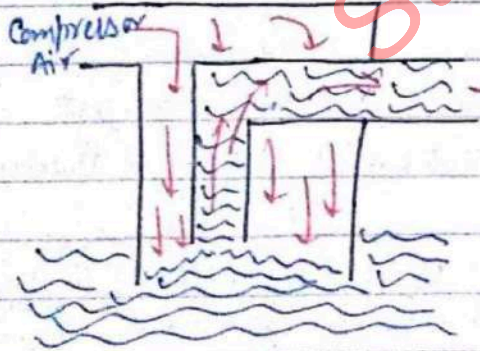
$$fe_2S_3 + 4O_2 \rightarrow 2feO + 3SO_2$$
(atmosphere)

$$4feO + O_2 \rightarrow 2fe_2O_3$$

LIQUID fUELS

PETROLEUM (Rock oil / Mineral oil , CV ≃ 40000 kJ/kg)

It is a complex mix of paraffin, olefinic & aromatic C_nH_y with small quantities of organic compounds containing O_2 , N_2 & S_2 .



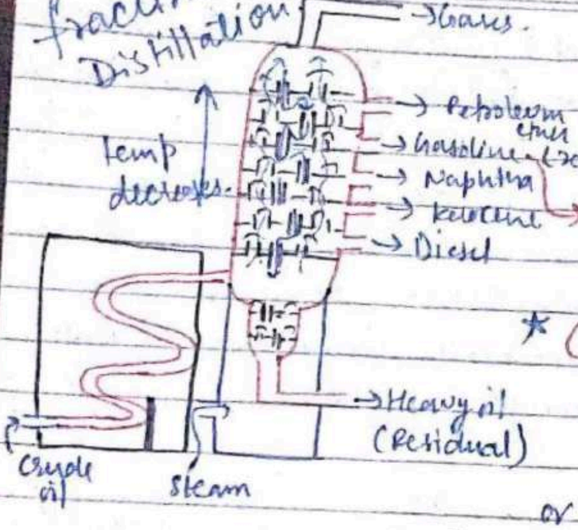
Refining of Petroleum

↳ Demulsification: (Cottrell's Process)
water is removed from oil by electrical Process. The crude oil is subjected to an Electric field, when droplets of colloidal water coalesce to form large drops which separate out from the oil.

↳ Removal of Harmful impurities.
Excessive Salt are removed by washing with water & objectionable sulphur are remove by treating oil with Cu oxide and then filter.

↳ fractional distilliation.

fractional Distillation



The separation of various fractions is based on the fact that the hydrocarbons of petroleum boil at different temperature

★ CRACKING: It is the process by which heavier fractions are converted into lighter fractions by the application of heat with or without catalyst.

$$\underset{B.pt = 170^\circ C}{C_{10}H_{22}} \xrightarrow{Cracking} \underbrace{C_5H_{12} + C_5H_{10}}_{B.pt = 36^\circ C}$$

$$C_8H_{18} \xrightarrow{cracking} C_5H_{12} + C_3H_6$$

Effect of cracking: ① Higher to lower Hydrocarbons ② High BP to low B.P ③ formation of Branched chain from straight chain ④ Unsaturated to saturated ⑤ Cyclization may takes place.

① Thermal Cracking: when cracking takes place simply by the application of heat and pressure. when Bigger HCs converted to smaller HCs. the thermal stability is as Paraffins < naphthenes < aromatics.

characteristic	Liquid-Phase T.C.	Vapour-Phase T.C
Type of oil	Any heavy oil	oil readily vaporises at low temp.
Cracking temp.	475 - 530°C	670 - 720°C
Pressure	100 kg/cm²	10 - 20 kg/cm²
Octane rating	65 - 70	> 70

★ Thermal cracking produces petrol which are less stable than straight run petrol due to presence of highly reactive unsaturated HCs in them.

Mechanism

Initiation: $CH_3(CH_2)_7CH_3 \xrightarrow{heat} CH_3(CH_2)_3\dot{C}H_2 + \dot{C}H_2(CH_2)_2CH_3$ (Thermally unstable)

Propagation:

$$CH_3-CH_2-CH_2-CH_2-\dot{C}H_2 \longrightarrow CH_3CH_2-\dot{C}H_2 + CH_2=CH_2$$

β Scission continues.

$CH_3-CH_2-\dot{C}H_2 \longrightarrow \dot{C}H_3 + CH_2=CH_2$

$CH_3(CH_2)_7CH_3 + \dot{C}H_3 \longrightarrow CH_3(CH_2)_5-\dot{C}H-CH_2-CH_3 + CH_4$

& $CH_3\dot{C}H_2 \longrightarrow CH_2=CH_2 + H^{\bullet}$ (No C–C bond β position)

Termination: $\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3$

$2CH_3-\dot{C}H_2 \longrightarrow CH_3-CH_2-CH_2-CH_3$

$CH_3-\dot{C}H_2 + \dot{H} \longrightarrow CH_3-CH_3$

② CATALYTIC CRACKING : Cracking is done at low temp & Pressure in presence of a catalyst. [catalyst → Zeolite]

ADVANTAGES of CATALYTIC OVER Thermal Cracking.

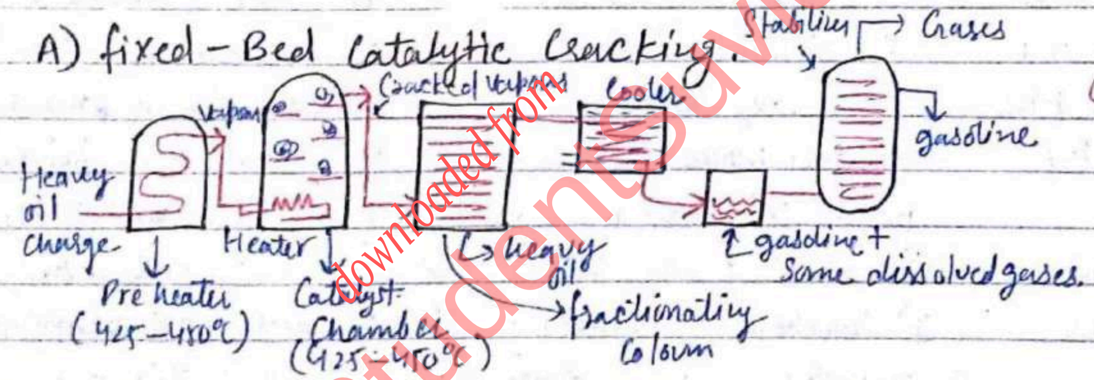
① Yield of gasoline is higher. About 70% of raw material is converted

② The gasoline contain low % of olefin & high % of isoparafin & aromatics. This inc. antiknock properties. and has octane number of 80.

③ The gasoline contains much less gum & gum forming compounds

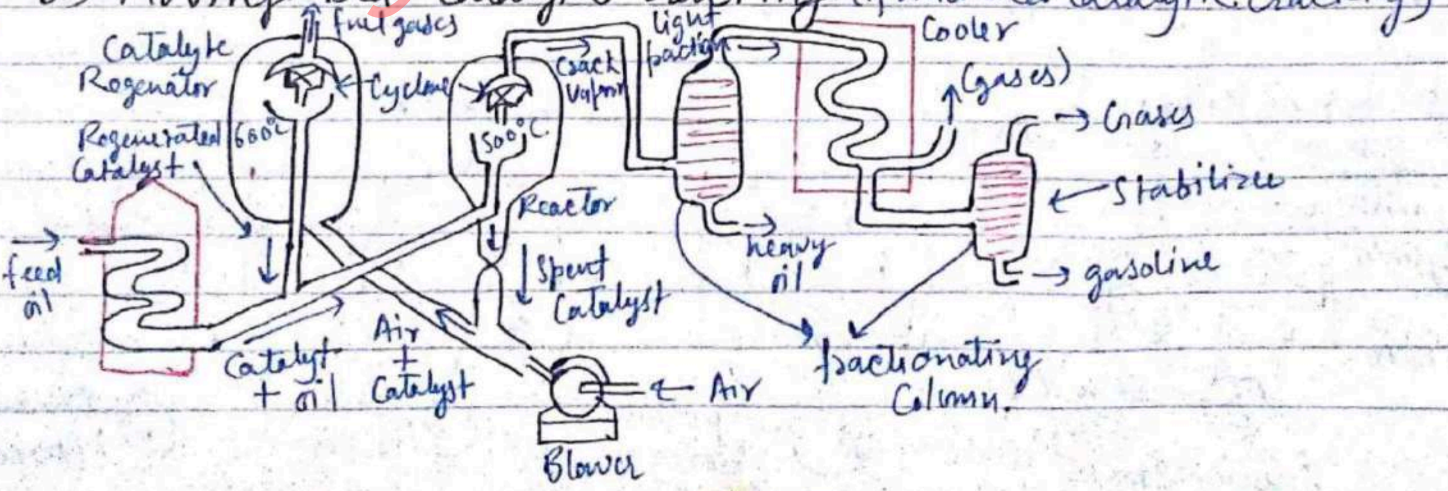
④ Yields less coke, less gas and more liquid Products.

A) fixed-Bed Catalytic Cracking.



Catalyste used (SiO$_2$·Al$_2$O$_3$) or bauxite, mixed with clay & zirconium oxide (endothermic rxns)

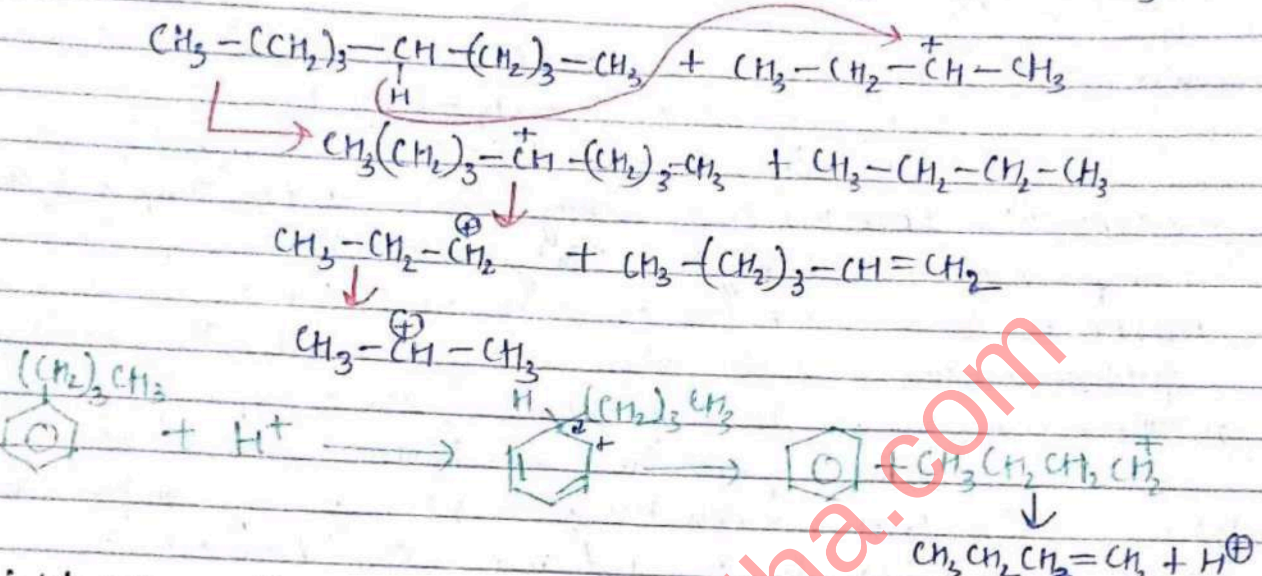
B.) Moving Bed Catalytic Cracking (fluid Bed catalytic cracking)



Mechanisms.

$$C_9H_{20} \xrightarrow{thermal} CH_3-CH_2-CH=CH_2 + C_5H_{12}$$

$$CH_3-CH_2-CH=CH_2 + H^+ \longrightarrow CH_3-CH_2-CH-\overset{+}{C}H_3$$



$$CH_3-(CH_2)_3-\underset{H}{CH}-(CH_2)_3-CH_3 + CH_3-CH_2-\overset{+}{C}H-CH_3$$

$$\longrightarrow CH_3(CH_2)_3-\overset{+}{C}H-(CH_2)_3-CH_3 + CH_3-CH_2-CH_2-CH_3$$

$$\downarrow$$

$$CH_3-CH_2-\overset{\oplus}{C}H_2 + CH_3-(CH_2)_3-CH=CH_2$$

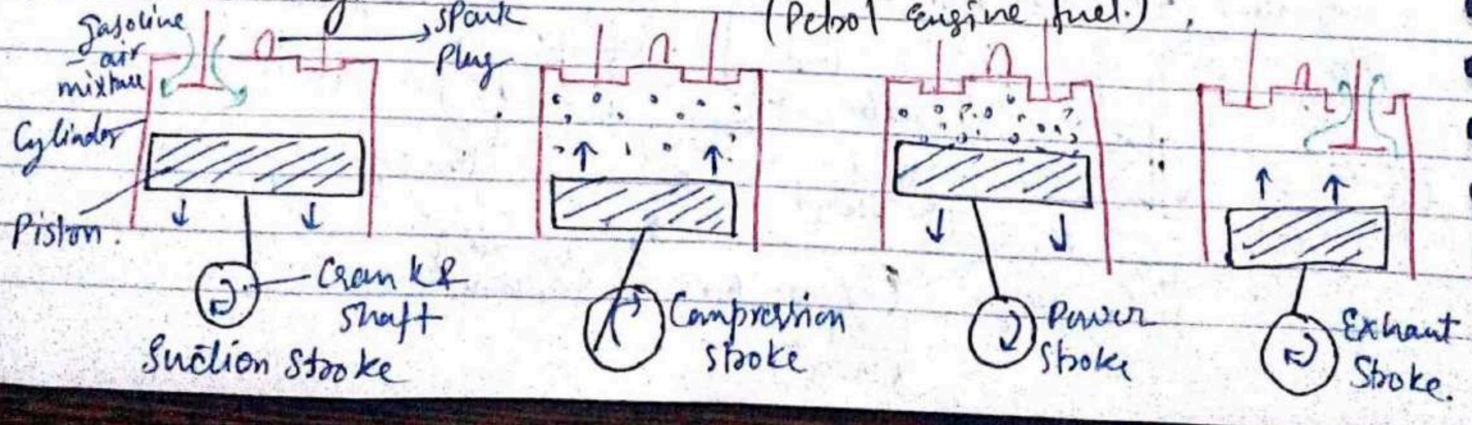
$$\downarrow$$

$$CH_3-\overset{\oplus}{C}H-CH_3$$

Straight-run gasoline	Cracked gasoline	Polymer gasoline.
① Obtained from Straight distillation of Crude Petrol	① obtained from heavy oil.	① obtained from Low molecular wgt components
② Physically Separated from crude oil	② Higher molecules are broken into lower molecules.	② Lower molecules are polymerised into higher molecules.
③ Low octane number	③ high octane no.	③ highest octane no.
④ Contains only normal alkanes	④ Contains aromatics, naphthenes & branched chain HCs	④ Contains more branched chains HCs
⑤ Composition range (C_5-C_9)	⑤ (C_6-C_8)	⑤ (C_7-C_8)

Knocking.

(Petrol engine fuel.)



* The ratio of the gaseous volume in the cylinder at the end of suction to the volume at the end of Compression. is termed as "Compression ratio"

↑ the Compression ratio ↑ is the efficiency of engine.

when. C.R. exceeds certain limits, mixture gets heated to the temp. greater Than ignition temp. & Spontaneous Combustion occurs even before Sparking. This is called "Pre-ignition" and also if last unburnt portion of mixture undergoes self ignition results in violence-explosion, This explosion produces a shocking wave, which hits wall of Cylinder & Piston and produce metallic Sound known as KNOCKING.

Knocking is thus a sharp metallic Sound similar to rattling of hammer which is produced in internal combustion engines due to immature Ignition of air-gasoline mixture. It dec. the efficiency of engine and Cause huge loss of energy and damage the cylinder & Piston.

→ knocking ↓ with ↑ in Compactness of molecules, double bond & aromaticity.

→ knocking ↑ with ↑ in length of HCs.

→ knocking ↓ with ↑ in branching & their positions.

Straight Paraffin > Branched Paraffin > olefin > cyclo paraffin > Aromatics

OCTANE RATING: It was observed that n-heptane knock badly (O.N – 0) and iso-octane has high Resistance to knock (O.N – 100)

"Octane number of a fuel is defined as the % of iso octane present in a mixture of iso-octane & n-heptane which has the Same knocking character as that of fuel under examination, under Same set of Conditions".

|Greater the O. No. Greater is Antiknocking Property|

Mix (80% isooctane & 20% n-heptane) ⟶ O.No. = 80.

Antiknocking Agent (Benzol & Alcohol, Tetraethyl lead (TEL))

Since TEL Converted to Pb & PbO which contaminate environment that's why C_2H_4Br is added, So that $Pb + C_2H_4Br \longrightarrow \underset{\text{(volatile)}}{PbBr_2} + CH_2=CH_2$

* Benzene is good Antiknocking Agent but Carcinogenic

Aviation Gasoline: Gasoline used in aeroplane as fuel. (O.No ≥ 100)

mix of iso-octane and 2ml TEL ⟶ O.No. 100+2.

* AKA - Anti-knocking Agent.

(Diesel Engine fuel)

① air is drawn in Cylinder and Compressed to a pressure of 30-50 kg/cm²
② Now diesel is injected in the form of fine droplets into very hot Compressed air. drops absorbs heat and izinite.
③ Pressure of gas evolved pushes the piston down (Power Stroke)
④ Exhaution Stroke.

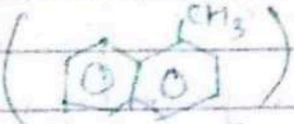
Knocking : The interval b/w The start of fuel injected and its ignition is termed as ignition delay or induction lag. when this lag is large. the fuel burns non-uniformly and violently. due to Sudden inc. in Temp. & Pressure. This is known as "diesel knocking. (↑lag ↑knock)

* Diesel engine should have low Spontaneous Ignition temp. to minimize the induction lag.

Cetane Rating : The Cetane number of a diesel oil maybe defined as The % of Cetane (n-hexadecome) [C.No. 100) in a mixture of Cetane and α-methyl naphthalene (C.No. 0) which will have The Same ignition characteristic as the fuel under test, under same set of Conditions.

Mix (45% Cetane & 55% α-Methyl Naphthalene) — C.No. 45

n-alkanes > naphthanes > alkenes > branched alkenes > aromatics



? why Good Petrol engine fuel is bad fuel for diesel engine & vice-versa

· In petrol engine pre-ignition by Compression leads knocking & hence fuel with high ignition temp are required. On the other hand in diesel engines ignition delay is The cause of knocking and the fuel with low ignition temp. is required.

DIESEL	PETROL
① cheaper, Compression engine	① Costlier, Spark ignition engine.
② fuel Consumption/unit Power produced is less	② fuel Consumption/unit Power Produced is more.
③ Exhaust gase contain lesser Pollutants	③ Contains more Pollutants
④ Combustion requires more expensive fuel injection device	④ Combustion requires simple Carburettor.
⑤ Alkyl nitrates, acetone (AKA)	⑤ TEL, Diethyl telluride (AKA)

COMBUSTION : It is a chemical Process accompanied by the liberation of heat and light. It is an exothermic reaction.

e.g. $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -97$ Kcal.

Ignition temperature : The minimum temperature at which the substance ignites and burns without further addition of heat from outside.

Calculation of Air required for Combustion.

	$C(s)$ +	$O_2(g)$ $\longrightarrow$	$CO_2(g)$
(By wgt)	12g	32g	44g.
(By vol.)	1 vol	1 vol	1 vol.

N & ash are non-Combustible and hence do not consume O_2 during Combustion.

Balanced rxn for most Common Component of any fuel.

- $H_2 + 1/2 O_2 \longrightarrow H_2O$
- $S + O_2 \longrightarrow SO_2$
- $CO + 1/2 O_2 \longrightarrow CO_2$
- $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$
- $2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$
- $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$
- $2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$

☆ Air Contains 21% of O_2 by vol. & 23% of O_2 by wgt.

Thus, $1 m^3$ of O_2 supplied by $\frac{100}{21} \times 1 = 4.76 m^3$ of air

$1 kg$ of O_2 supplied by $\frac{100}{23} \times 1 = 4.35 kg$ of air.

Mean molecular wgt of air is taken as 28.94 g/mol

☆ Min. O_2 required = Theoretical O_2 required − O_2 present in fuel.

(In case of incomplete Combustion, excess O_2 is calculated after substracting the amount of O_2 required to burn CO to CO_2)

☆ % of Excess of air = $\frac{\text{Actual air used} - \text{Theoretical air used}}{\text{Theoretical air}} \times 100$

☆ O_2 Present in fuel is in Combination with H_2 & the rest H_2 is available for combustion.

$$H_2 + 1/2 O_2 \longrightarrow H_2O + \text{Heat}.$$

Since 1 part H Combines 8 part of O

$\therefore$ Available H = $\left[\text{Mass of H} - \frac{\text{Mass of O}}{8}\right]$

$\therefore$ theoretical mass of O_2 required for complete combustion of 1kg of fuel = $\frac{100}{23}\left[\frac{32}{12} \times C + \frac{16}{2}\left[H - \frac{O}{8}\right) + S\right]$ kg.

Imp. $1m^3 = 1000L$

$22.4L = 1\,mole = 28.94\,g$ of air.

amount of air required (yL) = $\frac{28.94}{22.4} \times y$ g.

Imp. formula's for Numerical

Bomb-Calorimeter : $GCV = \frac{(W+w)[\Delta t + C.C] - (f.w.C + A.C)}{x}$

$NCV = GCV - 0.09\,H\,587$

Boy's Calorimeter : $GCV = \frac{W(\Delta T)}{V}$

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

Dulong's formula : $GCV = \frac{1}{100}\left[8080\,C\% + 34500\left[H\% - \frac{O\%}{8}\right] + 2240 \times S\%\right]$