ENERY FUELS

Fuel is a combustible substance with carbon as main constituent, which on burning in presence of air(combustion), produces large amount of heat. Thus heat can be used for domatic and industrial purpose. Eg:- wood, charcoal, coal, kerosenoil. During combustion of the fuel, the atoms of C, H, N combine with oxygen and liberate heat. The liberated heat is due to the difference in the energy of reactants and that of the products formed

$$\underset{\text{(more heat)}}{\text{Fuel} + O_2} \longrightarrow \underset{\text{(less heat)}}{\text{Products}} + \text{Heat}$$

Classification of fuels:-

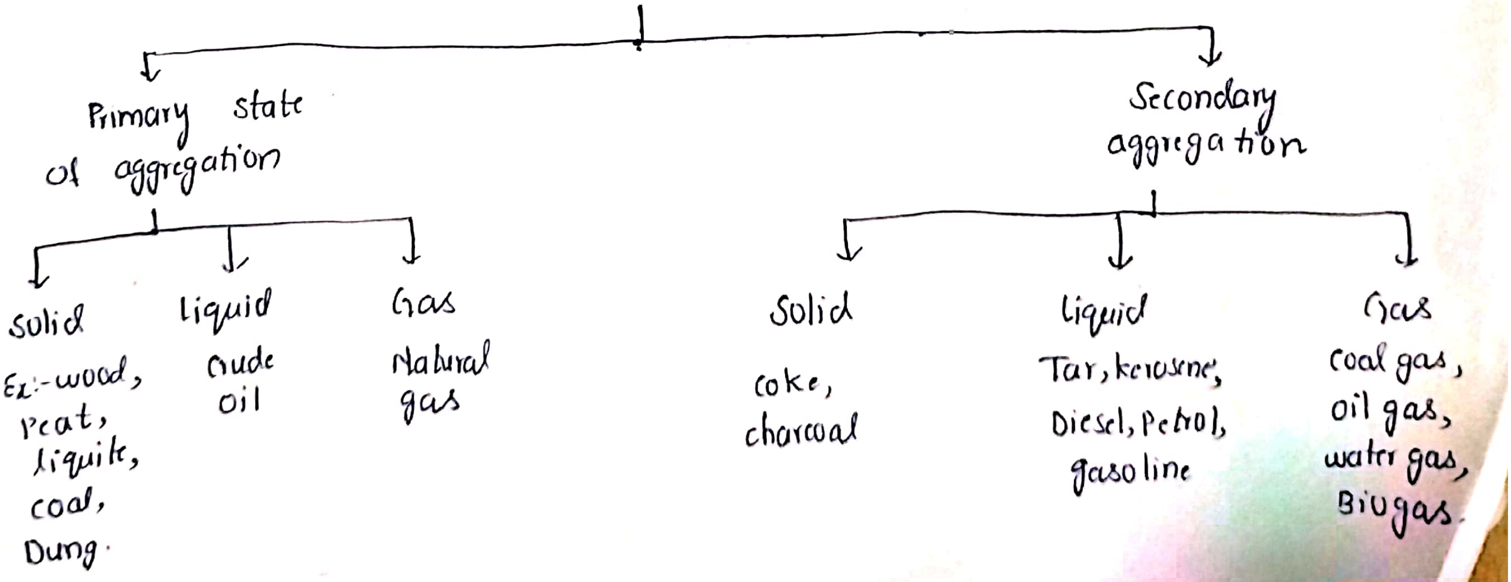
The primary source of fuels are coals and petroleum oils which are availiable in earth's crust and are called "fossil fuels";

Fossil fuels are classified according to their

1) occurence
2) state of aggregation

They are classified into : 1) Primary or Natural
2) secondory or artificial or derived

CHEMICAL FUELS OCCURENCE



The units are $Kcal/m^3$ or $B.Th.U./ft^3$
B.Th.U / cubic feet.

Characteristics of a Good fuel:

1) High Calorific Value: A fuel should have high calorific value.

2) Moderate ignition temperature: Ignition temp. is the lowest temp. to which the fuel must be preheated, so that it starts burning smoothly. Low ignition temp is dangerous for storage & transport of fuel. High ignition temperature is not helpful for ignition of fuel ∴ an ideal fuel should have moderate ignition temperature.

3) Low moisture Content: A fuel should have low moisture content as high moisture reduces the heating value.

4) Products of combustion should not be harmfu

5) fuel should be available in bulk at low cost.

6) Fuel must be easy to handle, store and transport

7) Combustion should be easily controllable

8) fuel should not undergo spontaneous combustio

9) Should burn in air with efficiency without much smoke.

10) fuel size should be uniform for regular combustio

Calorific value : -

→ Calorific value of a fuel is the total quantity of heat liberated when a unit mass / volume of the fuel is burnt completely.

Higher or Gross calorific value HCV :

HCV is the total amount of heat produced when a unit mass / volume of the fuel is burnt completely and the products of combustion are cooled to room temparature (15°c or 60°F).

Lower or Net calorific value :

LCV is the heat produced when unit mass / volume of the fuel is burnt completely and the products are permitted to escape.

$\therefore$ LCV = HCV − rate of heat of water vapour

= HCV − mass of $H_2 \times 9 \times$ latent heat of steam (5.87 kcal/kg)

i.e, 1 part by mas of H_2 produces a parts by mass of water.

Units :

Units of heat :

1) Calorie : It is the amount of heat required to raise the temp. of one g of H_2O thro 1°C

2) Kilo calorie : 1 Kilocalorie = 1000 calories. It is the quantity of heat required to raise the temp of 1kg of H_2O thro 1°C.

3 : British Thermal Unit B.Th.U : It is the quantity of heat required to raise the temp. of one pound of H_2O thro 1°F.

$$1 \text{ B.Th.U} = 252 \text{ cal} = 0.252 \text{ Kcal}.$$

$$1 \text{ Kcal} = 3.968 \text{ B.Th.U}.$$

Units of Calorific value :

Calorific value is expressed in Calorie/gram (cal/g) or Kilocalorie/Kg (Kcal/Kg) or (B.Th.U/lb) for solid or liquid fuel. In case of gaseous d chemical composition of fuel is

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

Natural fuels;

Wood

Wood is obtained from forests. Freshly cut wood contains 25-50% moisture. On drying, the composition of wood ~~is~~ is: C=55%. H=6%. O=43% Ash = 1%. Wood burns cv (calorific value) = 3500-4500 kcal/kg. Wood burns readily producing a long and non smoky flame & used as domestic fuel.

Coal

Coal is carbonaceous formed from vegetable matter. It consists of C, H, N, O.

$$\text{Wood} \rightarrow \text{Peat} \rightarrow \text{Lignite} \rightarrow \text{Bituminous coal} \rightarrow \text{Anthracite}$$

$\longleftarrow$ Moisture content, H, O, N, S, Volatile Matter

Carbon content, Calorific value, Hardness $\longrightarrow$

Origin of coal:

Geologist put forward two theories of coal formation

1) Insitu theory:

According to this theory, coal formation takes place at the place of vegetation itself.

2) Drift or Transportation Theory:

According to this theory, the trees were uprooted and transported by rivers to lakes where they get buried as huge piles of wood. Under high temperature, pressure, absence of O_2, presence of bacteria and time, the cellulose material of wood decompose with liberation of CO_2 & methane.

1. Peat

Peat is brown fibrous jelly like mass which is regarded as first stage in the coalification of wood. Composition: C = 57% H = 6% O = 35% ash = 2.5-6%. Cv = 5400 kcal/kg. Occur in Nilgiri hills

2. Lignites [brown Coals]:

Lignites are soft, brown coloured coals which consist of vegetable matter. C = 60-70% O = 20% It burns with long smoky flame Cv = 6500-7100 kcal/kg. Lignite deposits occurs in Assam, Kashmir, Rajasthan, Madras (at Neyveli).

3. Bituminous Coals [Common Coals]:

These are pitch black to dark green coals. They show a laminated structure of alternate very bright and dull layers.

Based on the Carbon Content, Bituminous Coals are classified as follows:

1) Sub-bituminous Coals:

hese are black, homogeneous, smooth in appearance with high volatile matter. On exposure to air, they rumble into small pieces. They are non-Caking coals with CV = 7000 kcal/kg. Carbon Content = 75-83% & O = 10-20%.

2) Bituminous Coal:

These show banded appearence with 90% Carbon and CV = 8000-8500 kcal/kg

3) Semi-Bituminous Coal:

These are rich in carbon 95% and has low volatile matter. CV = 8500-8600.

4. Anthracite:

It is the highest rank coal with 98% carbon. They are hardest of all kinds, quite dense, lustrous in appearence. They ignite with difficulty, burn without any smoke and give intense local heating. They have no Caking power. CV = 8650-8700 kcal/kg.

Analysis of Coal (X)

In order to assess the quality of Coal, the following two analysis are made.

1) Proximate Analysis
2) Ultimate Analysis

1. Proximate Analysis :

1. Moisture :

About 1g of dried & powdered coal sample is taken in a crucible and heated in an electric hot air oven at 105–110°c for 1hour. Then it is taken out, cooled in a desiccator and weighed. Loss in weight is reported as moisture.

$$\% \text{ of moisture} = \frac{\text{Loss in weight}}{\text{wt. of coal taken}} \times 100 .$$

Significance: Moisture lowers the calorific value of coal. Moreover, it quenches the fire in furnace. Hence lesser moisture content, better quality of coal as fuel.

2. Volatile Matter :

The dried coal sample left in the crucible is covered with a lid and placed in electric furnace at 925°c for 7 mts. Then the crucible is cooled in air and then in desiccator and weighed again. Loss in weight is reported as volatile matter.

$$\% \text{ volatile matter} = \frac{\text{loss in wt. due to removal of volatile matter}}{\text{wt. of coal sample}} \times 100$$

Significance :

High volatile matter means high proportion of fuel will distill over as gas or vapour and large amount will escapes unburnt. ∴ Coal with high volatile matter burns with long flame, high smoke and low calorific value.

3. Ash:

The residual coal in crucible is heated without lid in a muffle furnace at 700°c for ½ hr. The crucible is taken out, cooled in air and then in desiccator and weighed. This process of cooling, heating and weighing is repeated till constant weight is obtained

$$\% \text{ ash} = \frac{\text{wt of ash left}}{\text{wt. of coal taken}} \times 100$$

4. Fixed Carbon:

$$\% \text{ fixed Carbon} = 100 - \% \text{ of } \left[\text{moisture} + \underset{\text{Matter}}{\text{Volatile}} + \text{ash}\right]$$

Significance of Ash:

Ash is useless, non combustible matter which reduces calorific value. It also causes hindrence to the flow of air and heat, thereby lowering the temperature.

Significance of Fixed Carbon:

Higher the fixed carbon, higher will be the calorific value.

2) Ultimate Analysis:

1. Carbon & Hydrogen:

About 2g of weighed coal sample is burnt in presence of oxygen in combustion apparatus. C & H of the coal are converted into CO_2 & H_2O respectively. These gaseous products of combustion are absorbed in KOH & $CaCl_2$ tubes of known weights respectively. The increase in weights are determined.

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

$$\underset{12}{C + O_2} \longrightarrow \underset{44}{CO_2} \qquad \underset{2}{H_2} + \frac{1}{2} O_2 \longrightarrow \underset{18}{H_2O}$$

$$\% \text{ of } C = \frac{\text{increase in wt of KOH tube} \times 12}{\text{wt. of coal sample} \times 44} \times 100$$

$$\% \text{ of } H = \frac{\text{increase in wt. of } CaCl_2 \text{ tube} \times 2}{\text{wt. of coal sample} \times 18} \times 100$$

2) Nitrogen: Kjeldahl's Method:

About 1g of weighed powdered coal is heated with conc. H_2SO_4 with K_2SO_4 as catalyst in a long necked flask called Kjeldahl's flask. After the solution becomes clear, it is treated with excess of KOH and liberated NH_3 is absorbed in known volume of standard acid solution.

$$\% N = \frac{\text{Volume of acid used} \times \text{Normality} \times 14}{\text{wt. of coal taken}}$$

3) Sulphur:

Sulphur is determined in bomb Calorimeter where the sulphur present in the fuel, in presence of O_2, gets converted into SO_2. This on treatment with $BaCl_2$, gives $BaSO_4$ precipitate. This precipitate is weighed.

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

4. Ash

(as in proximate analysis)

5. Oxygen :

% of oxygen = 100 − % of [C + H + S + N + Ash]

Significance :

1. C & H Greater percentage of C & H, better is the quality & calorific value of coal.

2. Nitrogen

It has no calorific value. & hence it is undesirable.

3. Sulphur

Although it contributes to heating, its combustion products are harmful as they could corrode the equipment ∴ it is highly undesirable.

4. Oxygen :

It decreases the calorific value as they have high moisture ∴ undesirable.

Petroleum:

Petroleum or Crude oil is a dark greenish brown viscous oil found in earth's crust which is composed. of various hydrocarbons with small amount of N, O, S and the oil is found floating upon a layer of brine and has a gas layer on top. Composition: C = 79.5%. H = 11.5 – 14.8%. S = 0.1 - 3.5%. N + O = 0.1 – 0.5%.

Classification: Classified into 3 varieties:

1) Paraffinic base type Crude:

It is composed of saturated hydrocarbons from CH_4 to $C_{35}H_{72}$ with naphthalenes & aromatics. The hydrocarbons from $C_{18}H_{38}$ - $C_{35}H_{72}$ are semi solid called as waxes.

2) Asphaltic base type Crude:

It contains cycloparaffins or naphthalenes with little paraffins & aromatic hydrocarbons

3) Mixed base type Crude:

It contains both paraffinic & asphaltic hydrocarbon and rich in semi solid waxes.

Refining of Crude Oil:

The crude oil is separated into various useful fractio by fractional distillation & then converted into specific products. This process is called refining of crude oil and the plants set up for this purpose are called oil refineries.

The process of refining involves the following steps

Step 1: Separation of H_2O (Cottrell's Process):

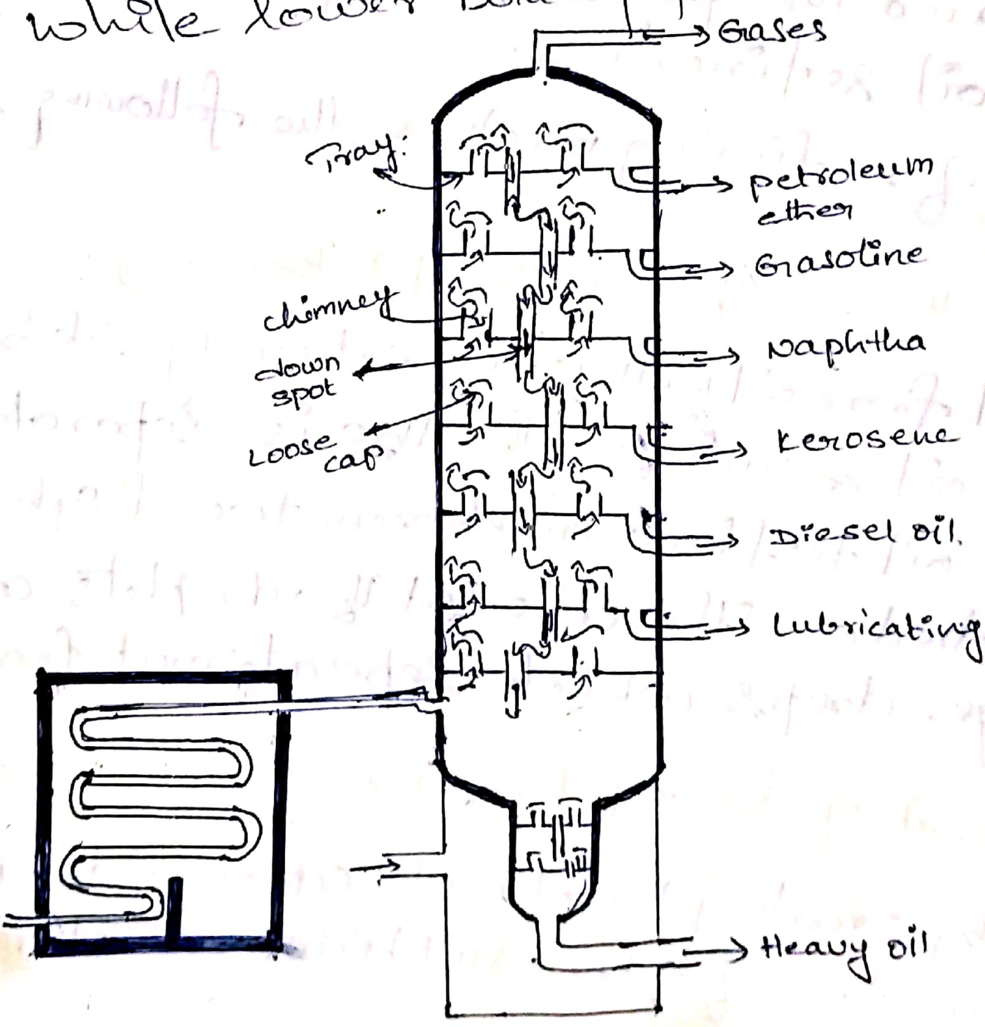
The crude oil from oil well is an extremely stable emulsion of oil & salt H_2O. The H_2O is separated by allowing the oil to flow inbetween two highly charged electrodes. The colloidal H_2O droplets combine to form large drops which separate out from oil.

Step 2: Removal of harmful Sulphur Compounds:

This is done by treating the oil with copper oxide which results in formation of copper sulphide which is removed by filtration.

Step 3: Fractional Distillation :

The crude oil is heated to 400°c in iron retort where all volatile constituents are evaporated. The hot vapours are then passed into a fractionating column. The column consists of a tall cylindrical tower containing a no/. of horizontal stainless steel trays at short destances. Each tray is provided with a small chimney with a loose cap. As the vapours go up, they become cooler & fractional condensation occurs at different heights of column. Higher boiling fractions condenses first while lower boiling fractions later.



Cracking : (x.)

Cracking is defined as the decomposition of bigger hydrocarbs. molecules into simpler, low boiling hydrocarbons of low molecular weight.

$$\underset{\text{Bpt} = 174^\circ C.}{C_{10}H_{22}} \xrightarrow{\text{cracking}} \underset{\text{n pentane}}{C_5H_{12}} + \underset{\text{pentene}}{C_5H_{10}}$$

Bpt = 36°C

Methods of Cracking:

1. Thermal Cracking
    - a) liquid phase thermal Cracking
    - b) Vapour phase thermal cracking
2. Catalytic Cracking
    - a) Fixed bed Catalytic Cracking
    - b) Moving bed Catalytic Cracking

1. Thermal Cracking :-

The heavy oils are subjected to high temperature & pressure, when bigger hydrocarbons are break down to give smaller molecules of paraffins, olefins & hydrogen.

This may be carried out into two ways:

a) Liquid Phase Catalytic Cracking :

The heavy oil are cracked at suitable temperature of 475-530°C under 10-20 kg/cm^2 pressure. The cracked products are separated in fractionating column. The yield is 50-60% & octane rating of petrol produced is 65-70.

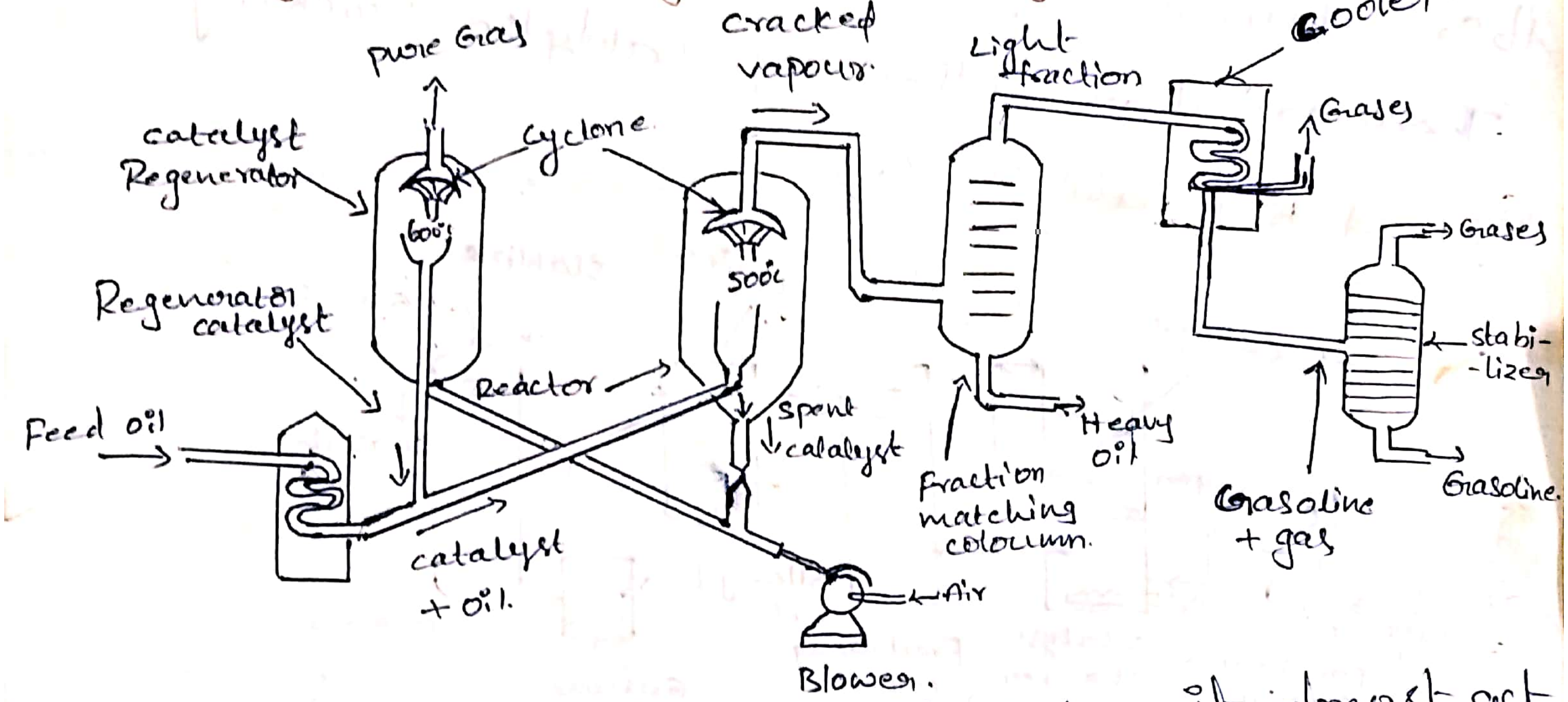
b) Vapour phase thermal Cracking :

The cracking oil is first vapourised and then cracked at 600-650 °C & at 10-20 kg/cm^2 pressure. This occurs in less time than liquid phase. Petrol obtained from this method has better anti knock properties but poor stability

2) Catalytic Cracking :

The quality & yield of gasoline produced by cracking can be improved by suitable catalyst like alumina Al_2O_3, aluminium silicate $Al_2(SiO_3)_3$ etc.

b) Moving Bed Catalytic Cracking :



The solid catalyst is finely powdered as it almost act like fluid, which can be circulated in gas stream. The vapours are mixed with fluidised catalyst and forced into reactor bed in which cracking of heavier into lighter molecules occurs. At the top of the reactor, there is a centrifugal separator called cyclone, which allows only the cracked oil hydrocarbons results :

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$$

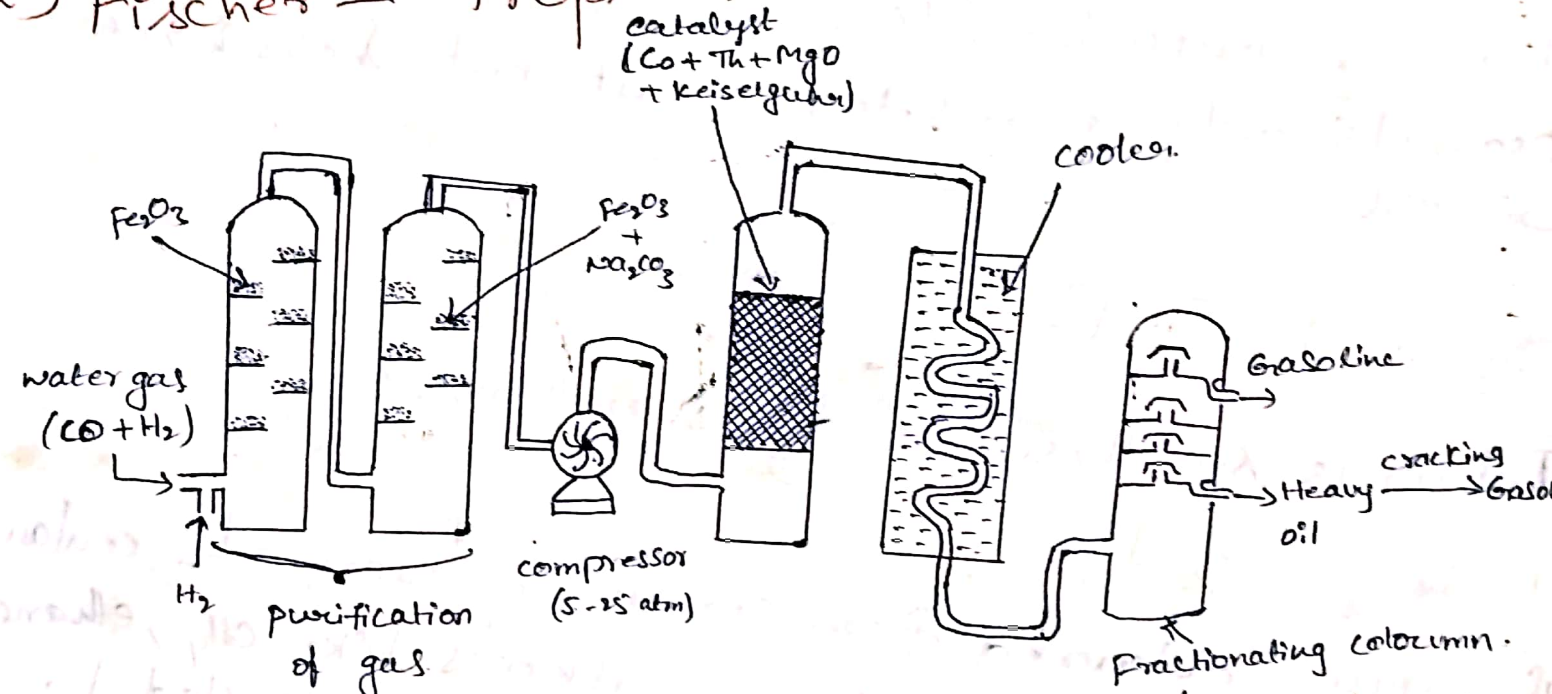
oil vapours to pass on to fractionating column but retains all catalyst powder in the reactor itself. The catalyst powder becomes heavier, due to coating with carbon & settles to the bottom from where it is forced by air blast to regenerator at 600°c.

In regenerator, Carbon is burnt & the regenerated catalyst then flows through stand pipe for mixing with fresh batch of incoming cracking oil. At the top of regenerator, there is a separator which permits only gases to pass out but hold back catalyst.

Synthetic Petrol :

Petrol is synthesized by 3 methods :

2) Fischer – Tropsch Method



water gas (CO+H_2), produced by passing steam over heated coke is mixed with H_2. The gas is purified by passing through Fe_2O_3 to remove H_2S & then to a mixture of Fe_2O_3 & Na_2CO_3 to remove organic sulphur compounds. The purified gas is compressed to 5-25 atm & then led to converted containing catalyst of 100 parts of cobalt, 5 parts of thoria, 8 parts of magnesia & 200 parts of keiselguhar earth at 200-300°C. A mixture of saturated & unsaturated hydrocarbons results :.

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$

$$nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O.$$

The reaction is exothermic, so the gaseous mixture is led to cooler. The crude oil obtained is further fractionated into gasoline, heavy oil. The heavy oil is reused for cracking to get more gasoline.

KNOCKING :

In internal combustion engine, a mixture of gasoline & air is used as fuel. After initiation of combustion reaction, by spark in the cylinder, the flame should spread rapidly & smoothly there by the expanding gas drives the piston down the cylinder.

The ratio of gaseous volume in the cylinder at th end of suction stroke to the volume at end of compression stroke of the piston is known as the Compression ratio. The efficiency of internal combustio engine increases with increase in compression ratio which depends on the nature of constituents present in gasoline.

In some cases, due to the presence of some Constituents in gasoline used, the rate of oxidation becomes so great that the last portion of fuel air mixture get ignited instantaneously producing an explosion. This is known as knocking which results in loss of efficiency.

The tendency of fuel constituents to knock is in th order: Straight chain paraffin > branched chain paraffi > olefins > cycloparaffins > aromatics.

Thus olefins of same carbon chain length posses better anti knock properties than the corresponding paraffins.