

**UNIT IV: FUELS**

Introduction-calorific value-HCV and LCV-problems using Dulong's formula-proximate and ultimate analysis of coal sample-significance of these analyses-problems-Petroleum (refiningcracking)-Synthetic petrol (Fischer Tropsch and Bergius)-petrol knocking-diesel knocking-octane and cetane ratings-anti-knock agents-Introduction to alternative fuels (Bio-diesel, ethanol, methanol, Natural gas, LPG, CNG)-Flue gas analysis by Orsat apparatus-Rocket fuels

**UNIT- IV**  
**FUELS AND COMBUSTION**

**FUELS**

- A fuel is a combustible substance which on proper burning in atmospheric air gives large amount of heat and energy which is used for domestic & industrial purpose.
- Fuel + oxygen -----→ product (CO<sub>2</sub> + H<sub>2</sub>O) + heat.
- The main components of any fuel are Carbon, Hydrogen, and sulphur and phosphorous as impurity.

**Classification of chemical fuels;-**

These are two types, Primary fuels – found in the nature .Secondary fuels—which are obtained from primary fuel.

Fuel physical state	Primary (or)natural fuels	Secondary (or) synthetic fuels.
• solid	Wood ,peat ,lignite, coal	Coke, semi coke, char coal
• liquid	Petroleum(crude oil)	Coal tar, petrol, deasil.
• gas	Natural gas	Coal gas, water gas, producer gas

**Calorific value:** - The amount of heat obtained by a complete combustion of a unit mass of a fuel.

Fuel calorific value is two types:-

- Gross calorific (or) higher calorific value (H.C.V)
- Net calorific value (or) lower calorific value (N.C.V)

**Gross Calorific Value – (G.C.V) :-**

- It is the total amount of heat produced when Unit mass of fuel is completely burned without elimination of latent heat of water vapour.

**Net Calorific Value – (G.C.V) :-**

N.C.V = gross calorific value – latent heat of vaporization. [Mass of hydrogen per unit weight of fuel burnt  $\times 9 \times$  latent heat of vaporization of water]

one part of H gives 9 parts of H<sub>2</sub>O and latent heat of steam for water is 587 cal/g.

$N.C.V = G.C.V - 9 \times (H/100) \times 587$       Where H = % of Hydrogen in the fuel)

(Or)

$N.C.V = G.C.V - 0.09 \times H \times 587$

## Solid fuels.

**Analysis of Coal:** - To assessment the quality of coal is proved by the following to analysis.

1. Proximate analysis
2. Ultimate analysis

**Proximate Analysis of Coal :** - Based on the determination of **% of moisture, volatile matter, ash and fixed carbon** in a given whole sample. This information gives to estimate the quality of coal.

**Moisture :-** Step-1 1 gm of air dried coal powder taken into crucible which is heated on electrical oven at 105 °C for 1 hour after cool in desiccators cool and weight out the weight loss represented as %moisture

**%moisture = loss in weight of coal/weight of coal taken  $\times 100$**

**Volatile matter:**

Step-2: dried coal left in crucible from step1 covered with lid which is heated on muffle furnace at 950c for 7 minutes and cool in desiccators and weighted out and the weight loss represented as % volatile moisture.

**% volatile matter = loss in weight due to removal of volatile matter/weight of coal taken ×100**

**Ash:** Step-3 the residual sample in crucible from step 2 which is heated again muffle furnace at 700 to 750 Oc The weight loss is represented as

**%ash=weight of residual/weight of coal taken×100**

**FIXED CARBON** – Fixed carbon is determined by the following equation

**% of fixed carbon = 100 - (% of the moisture + volatile matter + ash)**

Good quality of coal has more fixed carbon

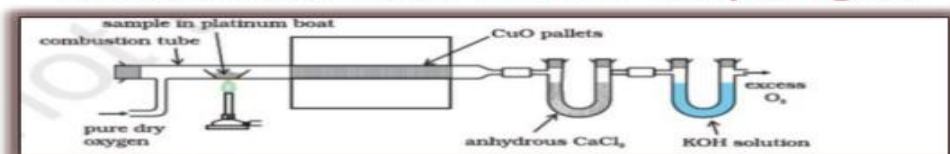
## Ultimate analysis of coal

Ultimate analysis of coal is determined by % of compositions of the elements or constituted of elements of carbon, hydrogen, nitrogen, sulphur, oxygen and ash content

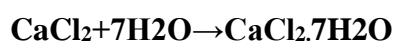
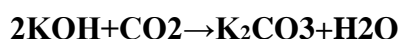
### Carbon and hydrogen % determination

- 1 -2 gm of coal sample is burnt in oxygen the coal sample containing carbon to give CO<sub>2</sub> and hydrogen to give water by the combustion.
- CO<sub>2</sub> passed through the KOH capillary Bulbs there by increased weight of that bulb corresponding to % of carbon
- H<sub>2</sub>O is passed through CaCl<sub>2</sub> bulb there by increased weight of that bulb corresponding to % of hydrogen

### Determination of carbon & hydrogen



- About **0.2g** of accurately weighed coal is burnt in oxygen in apparatus shown above.
- **C → CO<sub>2</sub> & H → H<sub>2</sub>O**
- KOH & CaCl<sub>2</sub> absorb CO<sub>2</sub> & H<sub>2</sub>O respectively.
- Increase in **weights** of the tubes are noted.



**%carbon = increased in weight of KOH tube/weight of coal taken × 12/44**

**%hydrogen = increased weight of CaCl<sub>2</sub> bulb/weight of coal taken × 2/18**

**Nitrogen:** % of nitrogen in coal determined by kjeldahl method

- A known weight of 1 gm of coal powder is taken in kjeldahl flask which is oxidized by heating with **H<sub>2</sub>SO<sub>4</sub>+K<sub>2</sub>SO<sub>4</sub> and HgSO<sub>4</sub>** to get clear solution of ammonium sulphate
- ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) which is followed by heating with KOH to liberate the ammonia (NH<sub>3</sub>) and added a known volume of HCl
- Which is titrated against with NaOH the amount of acid neutralised by liberated ammonia to determine the nitrogen

**% of nitrogen = volume of acid consumed × normality of acid × 14 × 100 / weight of coal taken × 1000**

**Sulphur:** sulphur present in coal is estimated by gravimetrically

A known coal sample burnt in bomb calorimeter, if sulphur is present to give sulphates, sulphides etc, which are followed by treatment with BaCl<sub>2</sub> to give the barium sulphate precipitation, and it is dried out and weighed out

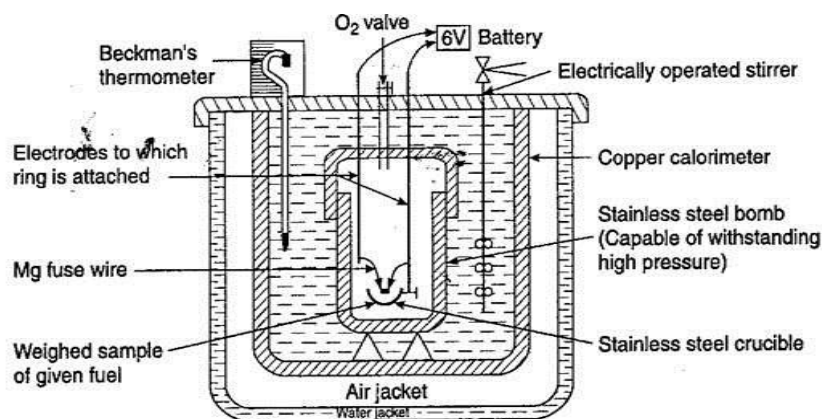
**% of the sulphur = weight of BaSO<sub>4</sub> × 32 × 100 / weight of coal taken × 233**

**Ash:** % of ash = weight of ash residue / weight of coal taken × 100

**Oxygen:** the percentage of oxygen is determined by subtracting sum of the percentage of C, H, S and ash from 100 % O = (100 - SUM of % C+H+N+S+ASH)

**% oxygen = 100 - % of (C+H+N+S+Ash)**

**Determination of solid or non volatile liquid fuel calorific value by bomb calorimeter**



- it consists of three racks(vassals) 1.steel bomb 2.copper calorimeter 3.Air jacket
- Steel bomb has tight with lid which contain two steel electrodes are connected to battery
- Steel bomb vessel is inserted into the copper calorimeter which contain the water, stirrer and Beckmann thermometer
- Coper calorimeter is also inserted into air jacket its main function to prevent the heat from outside

### **Procedure:**

- Take a known mass (0.5-1 gm) of the given fuel into crucible
- mg wire touch with sample passing the current through the electrodes
- Burning of the sample by the presence of  $O_2$  inside the steel bomb by the result of to release the heat
- liberated Heat from fuel is transferred to cu calorimeter there by water is heating slowly, when water temperature will get highest temperature recorded in thermometer which is indicated that fuel grass calorific value

### **Calculation:**

X=mass in gram of fuel taken crucible

W=mass of water in the calorimeter

w=water equivalent of the calorimeter, bomb, thermometer, stirrer

t<sub>1</sub>=initial temperature of water in calorimeter

t<sub>2</sub>=final temperature of water in calorimeter (after combustion)

l = higher calorific value(gross calorific value)

heat liberated by burning of fuel=(W+w) (t<sub>2</sub>-t<sub>1</sub>)

but heat liberated by fuel=heat absorbed by water apparatus

**XL= (W+w) (t<sub>2</sub>-t<sub>1</sub>)**

HCV of the fuel of= (W+W)(t<sub>2</sub>-t<sub>1</sub>)/X

Hence LCV=(L-0.09×H×587)Cal/gm

## **LIQUID FUELS**

### **PETROLEUM**

- Petroleum (fossil fuel or crude oil): it is the best primary liquid fuel---found in the deep earth crust (Petr a= rock, oleum = oil) ---- it is a brown viscous liquid
- it is the mixture of hydro carbons(paraffin ,aromatics ,naphthalene , nitrogen ,sulphur, oxygen

- The composition of crude oil is  $\rightarrow$  c-80-87%, s-0.1-35%, n-0.4-0.9%, h-11-15%, o-1-0.9%
- Refining of crude oil: Refining of crude oil involves the three steps:

### Step-1:

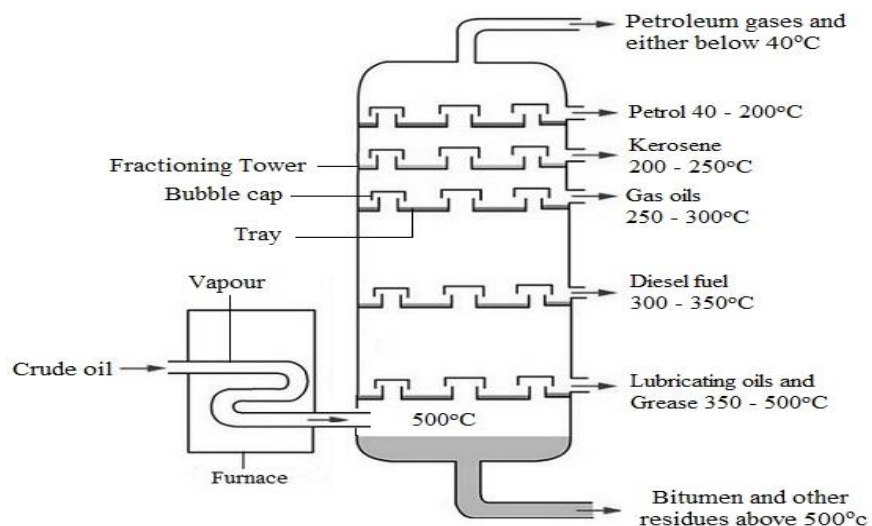
#### separation of water by coteril's method:

- The crude oil as an emulsion of oil and water .water is separated by using of highly charged electrodes ,the colloidal water is separated from oil in the form of big droplets by high current

### Step-2:

- **removal of sulphur compounds:**

Crude oil is treated with copper oxide ( $\text{Cu}_2\text{O}$ ) which gives black ppt o ( $\text{CuS}$ ) copper sulphte



### Step3: fractional distillation:

- Fractionating column consist of pipe still and bubble tower
- Bubble tower is a tall cylindrical tower containing number of horizontal trays, each tray provided the chimney, and covered with loose cap
- The crude oil is heated to 400°C in furnace (pipe still), converts into vapour
- The hot vapours are then passed into a fractionating column,
- As the vapours go up , through the chimney they become gradually cooler and fractional condensation takes place at different height of column

- Higher boiling point fractions condense first at lower part while lower boiling fractions condense above column. vapours, turn by turn different fractions are separated out at their corresponding boiling points

### **Rocket fuels:**

- Fuels which burn quickly and give a very large volume of gases to propel a rocket are called rocket fuel or propellants
- they are either high oxygen -containing fuels or mixture of fuel
- An oxidant the propellants reacts very quickly producing a very large volume of gases at a temperature of 3000c and a pressure of 300kg/cm
- The gases exit through a small opening call nozzle at supersonic velocity this act of pushing the gas backward produces equal force acting in the opposite direction which move the rocket forward rockets are used for putting space capsule into orbit and hurling explosives

### **Solid propellants:**

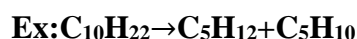
- EX: mixture of nitro cellulose and nitro glycerine
- mixture of nitro cellulose and nitro glycerine

### **Liquid propellants:**

- EX: hydrogen peroxide, nitro methane, ethylene oxide, hydrazine, propyinitrite and mixture of methanol and hydrogen peroxide

### **Cracking:**

Cracking is the process of conversion of bigger hydro carbon molecules into smaller hydro carbon of lower molecular weights (Decchene is cracking into pentane and pentene)



#### **Process of cracking brings about**

1. The conversion of high boiling fractions into low boiling fractions into boiling fractions suitable for automobile
2. production of raw material for petrochemical industries

**Cracking is mainly divided into two types -1. Thermal cracking 2. Catalytic cracking**

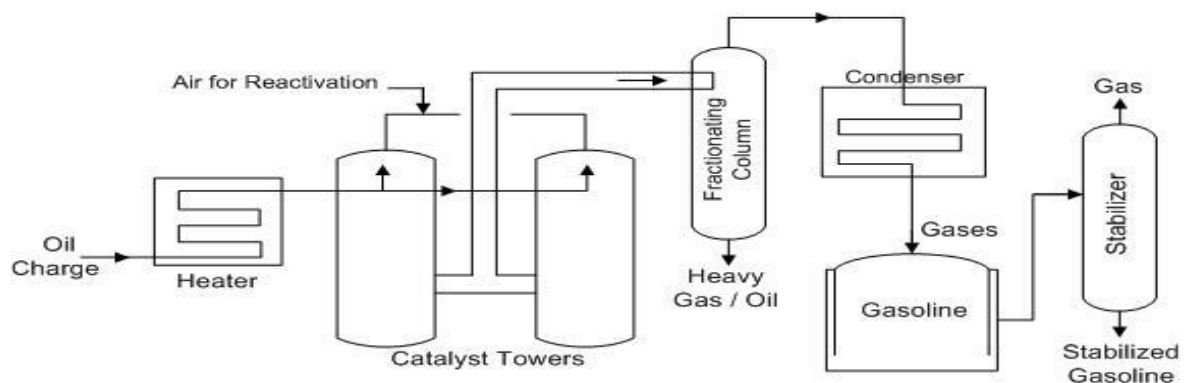
**Catalytic cracking: in this type cracking catalysts are used:**

- Suitable catalyst likes aluminium silicate,  $\text{Al}_2\text{O}_3$ , etc. by this catalyst cracking quality and yield of **Gasoline (petrol)** are produced. **By this Cracking process**

There are two types of catalytic cracking

1. Fixed bed catalytic cracking
2. moving bed catalytic cracking

### 1. Fixed bed catalytic cracking:



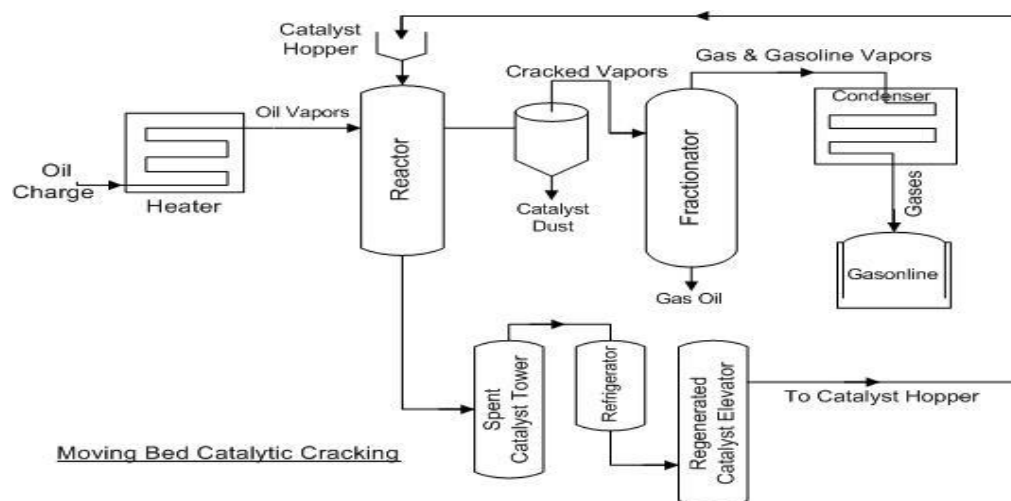
Fixed Bed Catalytic Cracking

- The oil vapour are heated in pre heater about  $425-450^\circ\text{C}$
- The hot vapours are forced to catalyst chamber (containing artificial clay+ $\text{zrO}_2$ ) maintained at  $425-450^\circ\text{C}$  and 1.5 kg/wt produced
- Cracking is taken place on catalyst bed 40% charge converted into petrol and along with 2-4% carbon dust produced dust deposit over the catalyst
- Cracked vapours produced are then passed through a fractionating column where heavy oil fractions are condensed
- The vapours are then passed through cooler where some gases are condensed along with gasoline uncondensed gases move on stabilizer where dissolved gases are removed and pure gasoline is obtained
- due to deposit of carbon dust over the catalyst bed after 8-10hour stops functioning bed is re activated by burning of carbon dust



## 2. Moving bed catalyst process (fluid-bed cracking)

- In this process the solid catalyst is finely powdered which act as a liquid and is circulated in gas stream
- Heavy oil vapours and catalyst fluid are allowed into reactor  $500^{\circ}\text{C}$  cracking is the takes place , near top of the reactor there is centrifugal separator, which can allow only cracked vapours but not catalyst powder and carbon dust
- Cracked vapours passed through fractionating column and heavy oil separated , formed vapours are sent to cooler gasoline is separate out along with uncondensed gases move on stabilizer
- Carbon coated catalyst reached at bottom of reactor and sent into regenerator and burnt at  $600^{\circ}\text{C}$  carbon dust elevated as  $\text{CO}_2$  and to produce freshly regenerated catalyst is reused



### Synthetic petrol or gasoline prepared by to process:

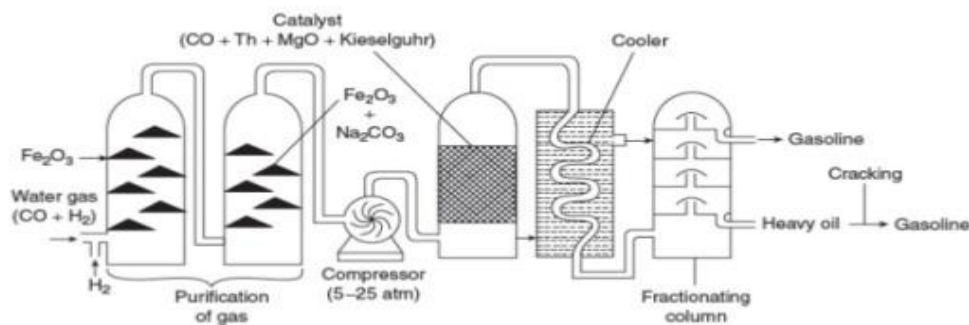
1. Fisher tropesch method
2. Bergius process

#### 1. Fisher tropesch method for synthetic gasoline (petrol)

- water gas is mixed with  $\text{H}_2$  gas, passed into purification towers to remove the  $\text{H}_2\text{S}$  and organic sulphur

- Purified gas is compressed at 5 to 25 atm are passed into converter containing catalyst mixture (a mixture 100 parts Co+5part thoria+8parts magnesia +200 parts kaisal gargh parts solution of earth) maintains at 200-300°C
- A mixture of saturated and unsaturated hydro carbons formed in the convertor
- $n\text{Co} + 2n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$ -----olefins
- $\text{C}_n\text{H}_{2n} + \text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2}$ -----paraffin
- Hot gas mixture passed into passed into a cooler where liquid resemble crude oil is obtained
- Crude oil sent into fractionating column to get gasoline and heavy oil, the heavy oil reused for cracking to get more gasoline

### Fischer-Tropsch Process

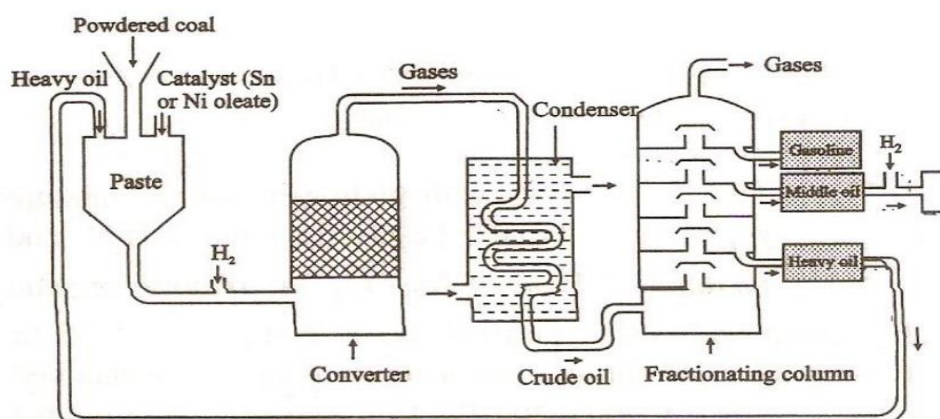


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## 2. Bergius process for Synthetic Petrol



- It is done by hydrogenation of coal
- low ash coal is powdered and mixed with catalyst (Ni) and made past by mixing with heavy oil
- The paste mixed with  $H_2$  gas and then sent through the converter which is maintained at  $350-500^\circ C$  and  $200-250^\circ C$
- The combustion of  $H_2$  with carbon coal to give hydrocarbon gases where liquid resembling the crude oil
- The gases coming out the convertor to pass the fractionating column where gasoline is obtained along with middle oil and heavy oil obtained.
- Middle oil and heavy oil are undergone by hydrogenation to give gasoline and heavy oil fraction as recycled to make as paste with coal powder

## **Internal combustion Engine properties:**

### **1. Knocking 2.antiknocking 3.octane number 4.cetane number**

#### **Knocking:**

- Knocking is un desirable properties of internal combustion engine
- When compression ratio is exceed then the normal way (to increase the rate of oxidation)
- By the result of to raise the temperature that causes for combustion of fuel before touch the spark ignition
- So that flame (combustion) leads to irregularly. randomly or,un uniformly thereby there is rattle sound generated the inside cylinder which is called knocking.
- Due to this property to reduce the piston life and damage the cylinder ,more consumption of fuel,
- This is mainly cause, to use the straight chain hydro carbon in petrol (chemical structure of hydro carbons)

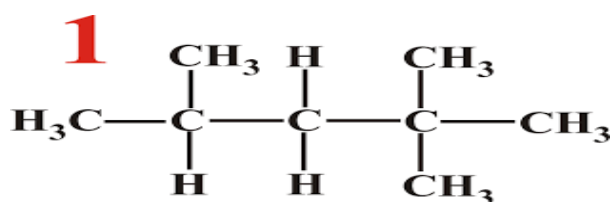
#### **Preventing the knock:**

1. Good quality of fuel with higher octane number
- 2.by adding anti knocking reagents
3. by the retarding sparkplug ignition

## Octane number:

- It is to be decided the quality of petrol it is introduced by edger he has to prove taken two components in gasoline
- n heptane →  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$  ( It shows 100% knocking (octane number=0)

### 1. 2,2,4 trimethyl pentane → *iso Octene*



(It shows 0% knocking (octane number=100))

### Octane number: Percentage of iso octane in mixture of isooctane+ heptanes

Octane Number = 80 means 80% iso Octane and 20% n heptane

The given fuel % n heptane - shows knocking

% iso octane- shows octane number

### Anti knocking reagents:

- Anti knocking reagents are added to straight chain hydro carbon petrol, which converts into branched chain hydro carbons there by knocking is reduced
- Petro anti knocking reagents are anti knocking reagents are –  $(\text{C}_2\text{H}_5)_4\text{Pb}$  tetra ethyl lead
- $(\text{C}_2\text{H}_5)_4\text{Pb}$  dissociate to give  $\text{C}_2\text{H}_5^-$  and  $\text{Pb}^{+2}$  radicals
- $\text{C}_2\text{H}_5$  able to attack the straight chain hydro carbon to converts into branched chain carbon
- During this process  $\text{pb}^{+2}$  is left over, which is poisoned and can be eliminated it by adding of  $\text{C}_2\text{H}_5\text{Br}$
- $\text{C}_2\text{H}_5\text{Br}$  is dissociated to give  $\text{C}_2\text{H}_5 + \text{Br}^-$  of the  $\text{Br}^-$  reacts with pb to give  $\text{pbBr}_2$  volatile

## Cetane number:

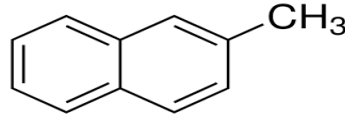
It is to be decided that the quality of diesel when diesel oil contain the branched chain hydro carbon shows knocking

**Disel Knocking:**

If branched or cyclic hydro carbon chain present in diesel (2 methyl naphthalene) it gives bad knocking but it contain straight chain hydrocarbon ( $\text{CH}_2\text{-(CH}_2\text{)}_{14}\text{-CH}_2$ ) does not exhibit the knock.

It is explained by use of the following compounds

Cetane –  $\text{CH}_2\text{-(CH}_2\text{)}_{14}\text{-CH}_2$  Hexadecchane



2 methyl naphthalene

Cetane number= % of **cetane in mixture of cetane+2 methyl naphthalene**

Ex: cetane number 60 means - 60% cetane 40 % 2methyl naphalene

It gives 40% knocking

**Anti knocking reagents for diesel:**

Anti knocking reagents like  $\text{CH}_3\text{-CO-CH}_3$ ,  $\text{C}_2\text{H}_5\text{NO}_2$  are added to diesel which contain cyclic structure are opened ring by ant knocking reagents to converts into straight chain hydrocarbon to reduce the knocking

**Natural gas:**

Natural gas primarily methane gas It is fossil fuel. it is two type:

1. Dry or lean gas: the natural gas contain  $\text{CH}_4$  lower hydrogen carbons like  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ etc---
2. Wet or reign gas: natural gas contain  $\text{CH}_4$  higher hydro carbons present

**Natural gas composition:**

It consists of 70 to 90%-  $\text{CH}_4$ , 5-10% ethane, 3-1 %  $\text{H}_2$  and react of Co and  $\text{CO}_2$  its calorific value 12000-14000 kcal/m

**Uses:**

1. Used as a domestic fuel, raw material in carbon block manufacture
- 2.It is used for manufacturing different synthetic chemicals
3. It is used in preparation of compressed natural gas
4. Due to less in preparation it is good substitute for petrol and diesel

**L.P.G : (LIQUID FIELD PETROLEUM GAS)**

1. The main components of 1 PG gas are n butane ,isobutene ,butylenes, and propane

- The gas can be compressed under pressure in container and sold trade flames like Indian, hp, bharat gas etc---
- The gas is obtained from natural gas or as a by product in refineries during cracking of heavy petroleum product
- its calorific value  $-27000 \text{ kcal/m}^3$

### Advantages of LPG

- LPG is used as domestic fuel and as fuel for internal combustion engine
- it is used in hydrolysis process
- LPG is used in industries as welding annealing ,cutting cl<sup>-</sup>

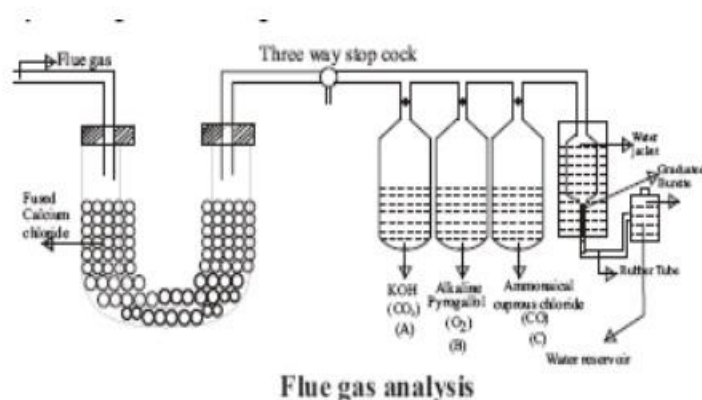
### C.N.G (compressed natural gas):

- When natural gas ( $\text{CH}_4$ ) is compressed at high pressure (1000 atm) or cooled to  $-160^\circ\text{c}$  it is converted in CNG
- it is stored in cylinder made of steel
- it is now replacing gasoline (petrol) as it releases less pollutants during combustion c.n.g vehicles are used to reduce the pollution

### Advantages:

- Due to high of ignition CNG is better than petrol and diesel
- It releases least pollutants like Co and un burnt hydro carbons
- Operating cost of CNG is less, and easily stored
- It undergo regular combustion

## ANLYSIS OF FLUE GASES BY ORSAT'S APPARATUS:



- Flue gases is mixture of  $\text{CO}_2$   $\text{CO}$ ,  $\text{O}_2$  exhausted from combustion chamber
- Analysis of flue gases the idea about complete or incomplete combustion process
- After combustion gases coming out  $\text{CO}_2$   $\text{CO}$   $\text{O}_2$  these are called flue gases
- in the case of **complete combustion** to evolve the  $\text{CO}_2$  gas, If **incomplete combustion** to evolve the  $\text{CO}$  will be more due to insufficient  $\text{O}_2$ . Excess oxygen supply to evolve the oxygen, it means more oxygen is supplied for combustion
- Orsat's apparatus is used for the flue gas analysis
- the apparatus has measuring with water jacket there are 3 absorption bulbs fitted with stop clocks and connections to measuring burette
- the bulbs are connected to **u tube** glass wool and fused  $\text{CaCl}_2$  which is to avoid incoming smoke particles to come in water jacket maintenance constant temperature in burette out of three bulbs
- first Bulb has  $\text{KOH}$  solution which is absorbed the  $\text{CO}_2$  in flue gases,
- The second bulb has alkaline pyrogallic acid which absorbs  $\text{O}_2$  and also absorb ( $\text{CO}_2$  if present)
- Third bulb has amonical  $\text{CuCl}_2$  acid it can absorb **CO** and ( $\text{O}_2, \text{CO}_2$  if present)
- . After each absorption in three bulbs the gas is sent from burette and the volume of gas is measured at room temperature the decrease in volume after each absorption corresponds to the volume  $\text{CO}_2$   $\text{CO}$ ,  $\text{O}_2$  in three bulbs the quantitative analysis of flue gas observed is made gas chromatography
- 12. The gas remaining in tube burette after absorption  $\text{CO}_2$   $\text{CO}$ ,  $\text{O}_2$  is taken as  $\text{N}_2$ , knocking the volume of gases observed and the volume of original gases, There % can be calculated.

% of the gas in the bulb  $\Rightarrow g = a / mv \times 100$ .

- Where  $a$ =amount of the gas in the bulb.  $m$ =mass of the gas in the bulb.
- $V$ =total volume of the gas in the bulb.

## Power alcohol;-

- Power alcohol fuel is used in powered car was made in china .in 1935
- ethyl alcohol is used in internal combustion engine as fuel it is called power alcohol
- Generally power alcohol 5-25% alcohol is mixed with petrol, and along with small percent of benzene
- Power alcohol has good anti knocking property with octane number =90 while petrol octane number =65

### Advantages:

- Increases the octane number of petrol
- Alcohol has a property of absorbing of water if present in pentane
- Power alcohol is cheaper than petrol

### Disadvantages:

- While power alcohol is used up to 35% power output is used
- Oxidation of ethyl alcohol produced acetic acid which causes corrosion to engine parts
- When power petrol is used to cause the starting troubles of making due to higher surface tension

## Bio-diesel:

- Bio diesel is chemically very similar to diesel and is produced by **transesterification of vegetable oil**
- Biodiesel molecules are long chain carbon atoms containing an ester group at one end. But diesel molecules does not have ester group
- Diesel engines can burn biodiesel fuel with no modification
- Vagatable oil molecules is three types larger than normal diesel molecules
- The large size of veg oil causes gels in cold weather this gel formation is prevented by biodiesel process. During this process elimination of H<sub>2</sub>O molecules otherwise to form soaps

