Syllabus Unit IV

Fuel Technology:

- **Solid Fuel- Characteristics, Significance of ultimate analysis of coal, concept of calorific value and its determination (GCV and NCV).**

- **Liquid fuel :Fractional distillation of crude petroleum, cracking of heavy oil**

- **Gaseous fuel: composition, characteristics and applications**

Energy I

Fuel –A fuel is the substance which on combustion produces a large amount of heat.

Calorific value

It is defined as the amount of heat obtained on complete combustion of unit mass of a solid or liquid fuel or unit volume of a gaseous fuel at STP.

Gross calorific value (G.C.V)

Gross calorific value of a fuel can be defined as the total amount of heat obtained on complete combustion of unit mass of a solid or liquid fuel or unit volume of a gaseous fuel (STP) and on cooling the products of combustion to $15\ ^0$ C. The gross calorific value is also called as higher calorific value.

The GCV is of only theoretical importance because in actual practice, we do not have any provision of cooling the products of combustion during combustion of a fuel in an engine, furnace or any other fuel burning device.

Net calorific value (N.C.V)

Net calorific value is defined as the amount of heat obtained practically on complete combustion of unit mass of solid or liquid fuel or unit volume of a gaseous fuel at STP and the products of combustion are allowed to escape with some heat .N.C.V is also called as lower calorific value.

A fuel containing hydrogen produce water vapours on combustion. Out of the total heat produced in combustion of the fuel, the water vapours take away a considerable portion of the heat and actually less heat is available for heating.

There is no furnace, engine or device designed to collect the heat being taken away by the water vapours. Therefore practically we get lower calorific value than the theoretically expected.

The N.C.V and G.C.V are related as under.

G.C.V=N.C.V+ (9 x h x latent heat of water/ 100)

Where h is the percentage of hydrogen in the fuel.

Units of calorific value

System	Solid/liquid fuel	Gaseous fuel
CGS	cal/gm	cal/lit
MKS	kcal/kg	$kcal/m^3$
S.I	joules/Kg	$joules/m^3$

The latent heat of water is 587 cal/gm or 2450 KJ/kg or 587 kcal/kg

Classification of Fuel :
1) Classification on the basis of occurrence:
    a) Natural or Primary fuel
    b) Artificial or secondary fuels
2) Classification on the basis of physical state
    a)Solid Fuel   b)Liquid Fuel   c)Gaseous Fuel

Solid fuels

Advantages
1. They are very cheap and easy to transport.
2. They can be stored safely as compared to liquid and gaseous fuels because they have a high ignition point.

Disadvantages
1. Lowest Calorific value (as compared to liquid and gaseous fuels).
2. They contain large amounts of non –combustible substances and therefore, produce ash and smoke.
3. Lot of space is required for storage.
4. Thermal efficiency is not so high. Heat is wasted by radiation and convection.
5. Their combustion is not easily controllable.

Liquid fuels

Advantages :
1) They have a high calorific value as compared to solid fuels.
2) They are ash less and smoke less and leave no residue.
3) They can be easily ignited, burn freely with a high efficiency and the required temp. can be easily attained.
4) They can be easily transported.
5) They require less space for storage.
6) They are clean in use and economic in labour.
7) They can be extinguished, when desired and hence there is no wastage.

Disadvantages:
1) They are inflammable and precautions must be taken during storage.
2) They give unpleasant and noxious odours on burning.
3) They need special devices for burning.
4) They are costly as compared to solid fuels.

Differences between solid and liquid fuels

Solid fuels	Liquid fuels
1. low calorific value	high calorific value
2. very high ignition temperature	moderate ignition temperature
3. high ash content	ash content is negligible
4. large volatile matter and moisture	volatile matter and moisture is negligible
5. velocity of combustion is non-controllable	velocity of combustion is easily controllable
6. required large space to store but no risk for fire hazard	required small space to store but risk for fire hazard
7. very low thermal efficiency	better thermal efficiency
8. burn with smoke	smoke is negligible
9. cannot be used in I.C. engine	convenient in I.C. engine
10. transportation is laborous but risk free	transportation can be piped but risky
11. cost is low	Cost is high

Gaseous fuels
Advantages
1. They have a high calorific value
2. They are ash less and smokeless
3. They are easy to ignite and extinguish
4. The combustion is uniform. Therefore, there is no loss of heat.
5. They can be transported through pipes.

6. Waste gases can be utilized for preheating gas and air.

Disadvantages

1. They are highly inflammable and the chances of explosion are more and fire-risk is more.
2. They require a large space for storage; therefore, large tank or containers are required.

3. They are more costly as compared to solid and liquid fuels.

Advantages of gaseous fuel over solid fuel

- . Gaseous fuel has higher calorific value than solid fuel.
- Gaseous fuels are clean in use and economic in labour as compared to solid fuels
- Gaseous fuels burns without smoke and ash formation.
- Combustion of gaseous fuels can be easily controlled by using regulators
- Gaseous fuels have high thermal efficiency than solid fuels.
- Gaseous fuels can be used in I.C. engines but solid fuels can not be used
- Gaseous fuels produces higher temperature than solid fuel.
- Gaseous fuels do not contain moisture or volatile impurities hence undergo complete combustion as compared to solid

Comparison of solid, liquid and gaseous.

Sr. No.	Criteria	Solid fuel	Liquid fuel	Gaseous fuel
1	Cost	Very cheap	Costly	Costly
2	Transportation	Easy& hazard free(because of high ignition temp/point)	Easy	Easy but risk of hazard.
3	Storage	Lot of space is required, safe storage	Smaller space is required	Large space is required for storage
4	Ignition point	Very high	Moderate	Very low
5	Calorific value	Low	Higher	Highest
6	Smoke(pollution)	Considerable	Lower	Nil
7	Thermal efficiency	Low	High	Higher
8	Examples	Coke coal	Crude oil, diesel oil kerosene etc.	Coal gas LPG etc.

Criteria for selecting a fuel:

The following criteria are taken into consideration for the selection of a fuel for a particular purpose.

1. The fuel selected should be most suitable for the process (For instance coke made out of bituminous coal is most suitable for blast furnace)

2. The fuel should possess a high calorific value.

3. The fuel should be cheap and readily available.

4. It should possess moderate ignition temperature.(Too high ignition temperature cause difficulty in kindling while too low ignition temperatures may create safety problems during storage, transport and use of the fuel.)

5. The velocity of combustion should be moderate.

6. The fuel should be such that a clean and safe operation is ensured.(too much smoke and obnoxious odours are not desirable.)

7. It should be safe, convenient and economical for storage and transport.

8. It should have low moisture content.

9. In case of a solid fuel, the ash content should be less.

Determination of calorific value of Solid, Non volatile liquid fuels by Bomb Calorimeter:-

The gross calorific value of solid fuels and liquid fuels can be determined by Bomb calorimeter.(If the liquid is volatile, then it is filled in a polythene capsule of negligible mass and then used in experiment).

Construction: A Bomb calorimeter consists of,

i)   Cylindrical bomb   ii) Calorimeter

iii) water and air jackets   iv) accessories   pellet press   Oxygen cylinder.

i) Bomb pot

 It is a cylindrical strong stainless steel pot having a lid. The lid can be fitted air tight to Bomb pot by screwing.

There are two electrodes fitted through the lid and there is an oxygen inlet valve at its centre

One of the electrodes is provided with a ring to hold the crucible containing fuel. There is a thin resistance wire tied to the electrodes in loop form and the loop touches the fuel.

The weighed fuel is burnt in the Bomb pot in the presence of high pressure oxygen.
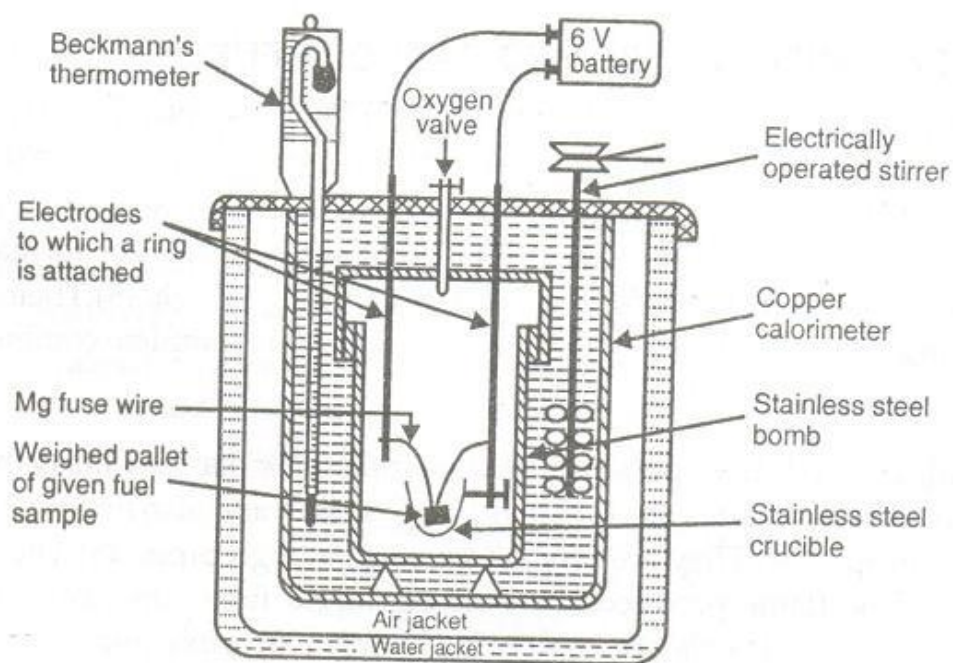
ii) Calorimeter:

There is a stainless steel or copper calorimeter in which the bomb pot is kept. It contains a known volume of water and the water is kept circulating around the Bomb pot with the help of a stirrer.

A Beckman thermometer or digital thermometer is kept in the water of calorimeter which can record the rise in temperature of water due to absorbing heat generated in burning of fuel in bomb pot.

iii) Water and air jackets:

The calorimeter is surrounded by air jacket and water jacket to avoid heat losses due to radiation.

There are insulator stands between calorimeter and water jacket.

Fig :-Bomb Calorimeter

iv) Accessories

There is a pellet press to convert the powder of solid fuel to pellet form. For a liquid fuel, a capsule of negligible weight can be used.

There is a oxygen cylinder with pressure gauge to fill oxygen in the Bomb pot at the pressure of nearly 25kg/cm2.

There is also a D.C battery of about 6 volts, to start combustion of fuel.

A piece of cotton thread which is tied round the wire required for igniting coal.

Working

i) Weigh the pellet of solid fuel or liquid capsule and keep it in the crucible. Keep the crucible in the ring of the electrode. Keep the resistance wire touching to the fuel.

ii) Add about 10ml of distilled water at the bottom of bomb pot and fix the lid tightly to Bomb by screwing.

iii) Fill the Bomb with oxygen at the pressure about 25 kg/cm2

Iv) Place the bomb in calorimeter. Add known volume of water in the calorimeter so that the bomb gets immersed in the water.

V) Place the calorimeter in the water jacket over the plastic studs. keep the thermometer and stirrer in the water of calorimeter.

vi) Put the plastic cover on the top and make electrical connections from battery to electrodes.

vii) Operate the stirrer for 5 minutes and note the initial temperature of water.

viii) Pass the current for about 5-10 seconds to heat the wire so that the fuel catches fire. If the fuel contains S and N elements, they get converted to SO_3 and N_2O_5.These gases get dissolved in the distilled water in Bomb to form H_2SO_4 and HNO_3 (along with liberation of little heat).

IX) Note the maximum temperature reached. After that note the rate of fall of temperature per minute and the time taken for reaching to initial temperature are noted.

X) Open the Bomb pot and wash the contents at its bottom into a beaker to find out the amount of H_2SO_4 and HNO_3 formed.

Calculations:-

Let, mass of fuel in gm = x gm

Mass of water in calorimeter = **W** gms

Water equivalent of calorimeter set = w gms.

Gross calorific value of fuel = L calories /gm.

Rise in temperature of water = (t_2-t_1)

Heat liberated by burning fuel=Heat absorbed by water and calorimeter.

So, x L= $(\mathbf{W} + w)(t_2-t_1)$

So G.C.V = $\mathbf{L} = \dfrac{(\mathbf{W} + w)(t_2-t_1)}{x}$ cal/gm.

Note:- water equivalent of calorimeter-set (w) is determined by burning fuel of known gross calorific value and using the above equation.

Standard gross calorific value of some pure fuels are,

S.N	Fuel	Standard gross calorific value
1	Naphthalene	9622 cal/gm
2	Camphor	9292 cal/gm
3	Benzoic acid	6325 cal/gm
4	Salicylic acid	5269 cal/gm

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NCV for the fuel is calculated as below:

If H is percentage of hydrogen in the fuel, then the heat taken by water formed during combustion to convert it into steam is = 0.09 H x 587 cal/gm.

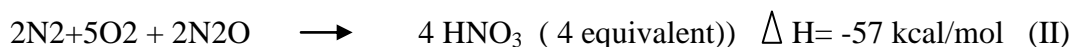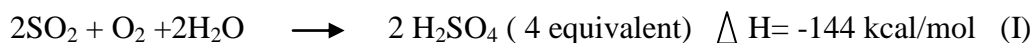**And NCV=GCV-0.09H x 587 cal/gm or Kcal/kg.**

Latent heat of vaporization of water = 587 cal/gm or kcal/kg.

CORRECTION :- To get more accurate results, the following corrections should be considered.

    i)   Fuse wire correction (f)
    ii)   Acid correction (a)
    iii)   Cooling correction (t_c)

i)   **Fuse wire correction (f):-**Out of the total heat obtained, little heat is given out by fuse wire when the current is passed for 5-10 sec. to start the combustion. Hence it must be subtracted.

ii)   **Acid correction (a):-**The S and N, in the fuel are oxidized to H_2SO_4 and HNO_3.formation of H_2SO_4 and HNO_3 are exothermic and the heat measured includes a small share by these acids formations.

$2SO_2 + O_2 + 2H_2O \longrightarrow 2\ H_2SO_4$ (4 equivalent) $\triangle$ H= -144 kcal/mol   (I)

$2N2 + 5O2 + 2N2O \longrightarrow 4\ HNO_3$ (4 equivalent)) $\triangle$ H= -57 kcal/mol   (II)

These two reactions are exothermic therefore correction must be made for heat liberated in the bomb by formation of H_2SO_4 and HNO_3.

3.6 calories should be subtracted for each ml of N/10 H_2SO_4 formed as per at equation (I).

1.43 calories should be subtracted for each ml of n/10 HNO_3 formed as per equation (II)

iii) **Cooling correction (tc)** :- If the time taken for water in calorimeter to cool from maximum temperature attained to the room temperature is t minutes and average cooling rate is dt/min, then the cooling correction to be added to rise in temperature is t.dt.

The cotton thread used for firing the charge also produces heat on combustion which is to be subtracted from total heat. For each gm of cellulose 4140 cals must be subtracted.

The actual rise in temperature would have been (t2-t1+ t.dt),had the heat liberated been absorbed by water and calorimeter rapidly and there would have no loss of heat from the set by radiation. the wall of the stainless steel bomb is very thick and stainless steel is not so good conductor of heat. Therefore the heat generated in the bomb is not transeferred to water rapidly and the temperature of water in calorimeter rises to lower value than expected.

The accurate formula for GCV is,

$$L = \frac{(\mathbf{W} + w)\ (t2\text{-}t1 + t.dt)\text{- }(\ a + f + c)}{x} \qquad cal/gm$$

Boy's calorimeter:

This calorimeter is used to measure calorific value of gaseous fuels and highly volatile liquid fuels.
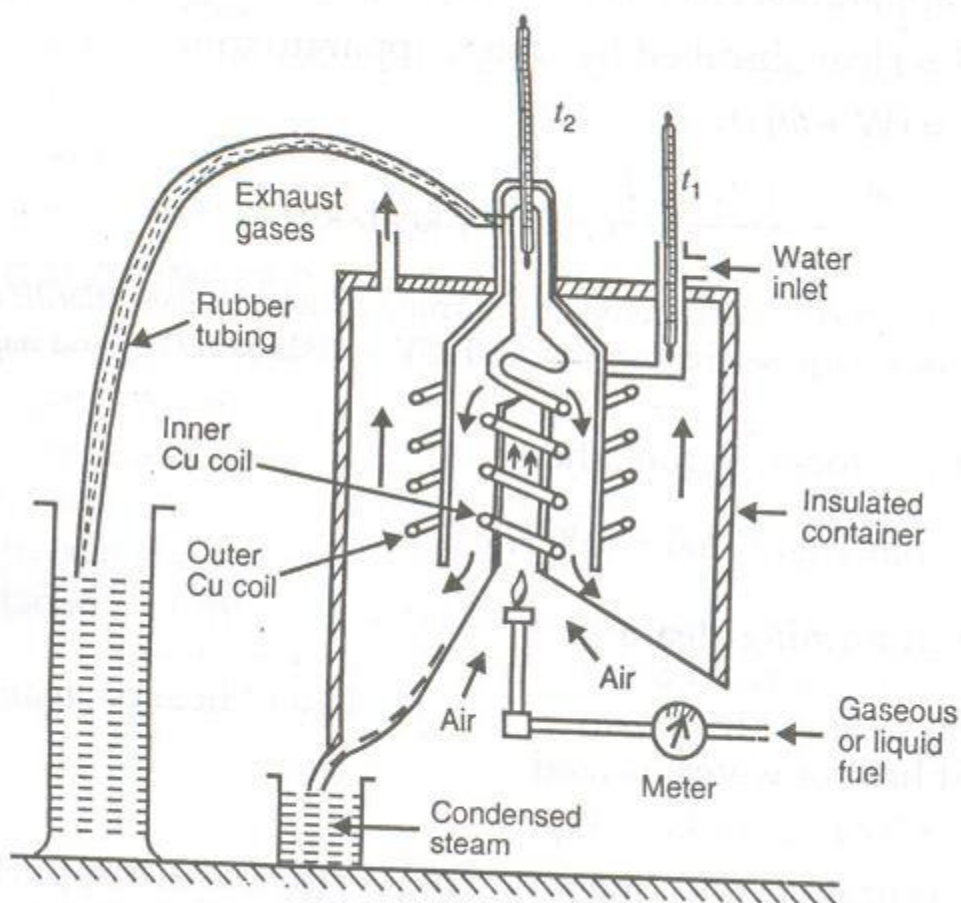
Principle:

A gaseous fuel is burnt at a known constant rate in the calorimeter under such conditions that entire amount of heat produced is absorbed by water, which is also flowing at a constant rate.

Construction:-

It consists of following things:

i)   Gas burner
ii)   Combustion chamber (Chimney)
iii)   Thermometers
iv)   Insulating cover

Fig:-Boy's calorimeter

I)Gas burner: There is a gas burner in which a known volume of gas is burnt at a known pressure. The gas is burnt at the rate of 3-4 lit. per minute.

II) combustion chamber (chimney) **A**round the burner there is a combustion chamber which has a copper tubing coiled inside as well as outside of it. Water enters from top of the coil, moves to bottom of chimney and goes up through the inner coil to the exit at top.

Iii)Thermometers: There are two thermometers to measure temperatures of inlet water and outlet water.

Iv)insulating cover:-The assembly is covered with by an insulator to detach combustion chamber from atmosphere. There are three holes, for exhaust gas, water inlet and condensed steam.

Working

I) start burning the gas at suitable pressure and adjust the rate of water flow such that the temperature of outgoing water remains constant.

ii)Burn the gas for 5-10 minutes to have the steady temperatures in and around the combustion chamber.

iii)After the steady conditions of outgoing water temperature, constant water circulation and gas flow reached, simultaneously note the following;

A) volume of gas burnt at given temperature and pressure in certain time period.

B) quantity of water passed through coil during this period.

C) mass of water condensed from product gas during the period.

D)The steady rise in temperature of water (t2-t1)

Calculations:-

I) First convert the volume of gas burnt to volume of gas at STP. let this STP volume be V m3.

Ii) Let, W=mass of cooling water used in the period of observation, in Kg.

Iii)Let m=mass of water condensate in kg.

Iv)L=G.C.V of the fuel.

Heat produced by combustion of fuel=heat absorbed by cooling water.

v)   (assuming no heat loss, in the steady state conditions)
vi)   So, VL=W(t2-t1)
vii) So, L=w(t2-t1)/V   kcal/m3
viii) The mass of condensate water per m3 of gas will be m/V kg/m3.
ix)   If this water had left as steam in product gases, it would have taken away heat=m/V x 587 kcal/m3
x)   So NCV=GCV-m/v x 587

$$NCV = \frac{W\,(t2\text{-}t1)}{V} \;-\; \frac{m \times 587}{V} \quad Kcal/m3$$

Solid Fuels

Stages of coalification of wood:

Wood ⟶ Peat ⟶ Lignite (Brown coal) ⟶ Bituminous coal ⟶ Anthracite coal

As the coalification progresses, the percentage of carbon and hardness increases, while the percentage of hydrogen, oxygen, moisture and volatile matter generally decreases.

Variation in average composition from wood to anthracite during different stages of coalification

Fuel	Moisture at 40 º C and 60% relatives humidity	Volatile matter	C	H	N	O	Calorific value MJ/Kg (1MJ/kg=238.8 kcal/kg)	Application
Wood	25	75	50	6	0.5	43.5	20.9	Used as a domestic fuel.
Peat	25	65	57	5.7	2.0	35.3	23.0	For domestic appliances, for steam raising, for thermal insulation.
Lignite	18	50 to 56	67	5.0	1.5	26.5	27.2	.As fuels in power plants and in the form of briquettes for domestic use
Bituminous Coal	4	20 to 45	83	5.0	2.0	10.0	36.0	Used for domestic and industrial purposes. For manufacturing coke and gas production, by product manufacture.
Anthracite coal	1.5	5.6	9.3	3.0	0.7	3.0	35.6	In metallurgical operations, for manufacture of cathodes for aluminium industry and as a filter medium of water treatment.

Analysis of coal

The composition of coal varies widely from mine to mine and hence it is necessary to analyze and interpret the results from the points of view of

Commercial classification (To determine quality)

Price fixation

Proper industrial utilization

Calculation of theoretical calorific value.

Types of analysis

The quality of coal is ascertained by the following two types of analysis

1) **Proximate analysis**, which includes the determination of moisture, volatile matter, ash and fixed carbon. This gives quick and valuable information regarding commercial classification and determination of suitability for a particular industrial use.
2) **Ultimate analysis**, which includes the estimation of carbon, hydrogen, nitrogen, sulfur, ash and oxygen.

Significance of ultimate Analysis

Carbon- It increases the calorific value, so its higher % is preferable.

Nitrogen – It is non- combustible so should be present in low amounts in fuel.

Hydrogen- It may be present in combination with O_2 or volatile matter. It decreases the calorific value of coal. So its % in general should be low.

Sulfur –It increases the calorific value but produces harmful gas (SO_2 and SO_3) Sox pollution and causes acid rain, corrosion of metallic equipment so its amount should be low.

Ash-It is non- combustible, so should be less.

Oxygen- Higher the % of O_2 more is the capacity of coal to hold moisture. It decreases the calorific value of coal so it should be less.

Difference between Proximate analysis and Ultimate analysis

S.N	Proximate Analysis	Ultimate Analysis

1	It consist of determination of moisture, V.M, ash, content of fixed carbon in coal	It consist of determination of % of C, H, N, S of coal
2	It indicates the amount of non combustible substance in coal	It does not indicate the amount of non combustible substance in coal
3	It does not indicate the pollution due to sulphur in coal	It indicates the pollution due to sulphur in coal
4	It is cheap analysis	It is costly analysis

Liquid Fuels

Petroleum

Petroleum or crude oil is the main source of liquid fuels. It is also known as rock oil or mineral oil. It is a dark coloured viscous liquid found deep in the earth's crust. It is a complex mixture of hydrocarbons (e.g paraffinic, olefinic and aromatic) with small quantities of optically active organic compounds containing O,N and S and traces of metallic costituents.

The average composition of crude oil is as follows

C   80 to 87.1%

H   11.1 to 15 %

S   0.1 to 3.5 %

O   0.1 to 0.9 %

N   0.4 to 0.9 %

Refining of petroleum

The process by which the crude oil is freed from its impurities, separated into various fractions having different boiling points and further treated to remove undesirable tendencies and to impart specific properties in them is broadly known as "Refining of petroleum."

Working

The crude oil is heated to about $400\ ^{0}C$ in a furnace & hot vapours coming out are passed near the bottom of the tower.

The tower is hot at the lower end & comparatively cooler towards the upper end. As the vapours of the oil   rise up in the fractionating tower, they gradually cooled & fractional condensation takes place through chimneys in trays at different heights of columns. The highest

boiling fraction condense at the bottom & the lowest boiling fraction condense at the top. The outlets are attached at the side of the column at suitable heights to withdraw a number of fractions.

The residue left in the retort above 400 ^{0} C is a black and tarry mass called 'asphalt or pitch' .It is used for making paints and as a preservative for wood and metals. It is also used for metalling of roads.

Fig. Fractionating tower
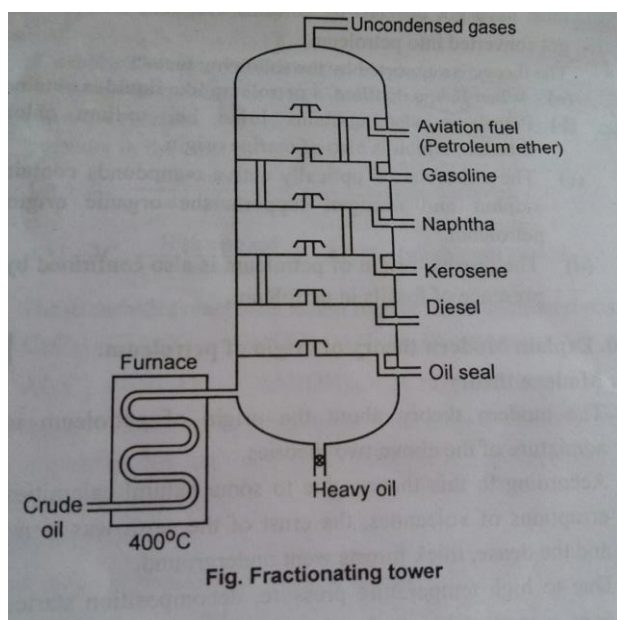
The different fractions of petroleum and their uses are discussed as follows.

Sr.No	Name of fraction	Boiling range	Composition of hydrocarbon	Uses
1	**Uncondensed gases**	Below 40^{0}C	C_1 to C_4	Domestic & Industrial fuel under LPG
2	**Aviation fuel or petroleum ether**	40-70^{0}C	C_5 to C_7	Fuel for aeroplane, helicopters, as solvent
3	**Petrol or gasoline**	70-120^{0}C	C_5 to C_8	Fuel for petrol engine, dry cleaning ,as solvent
4	**Naphtha or solvent spirit**	120 -180 ^{0}C	C_7 to C_{10}	As solvent and for dry cleaning
5	**Kerosene**	180-250 ^{0}C	C_{10} to C_{16}	For illuminating domestic fuel, for oil gas and fuel of jet engines.

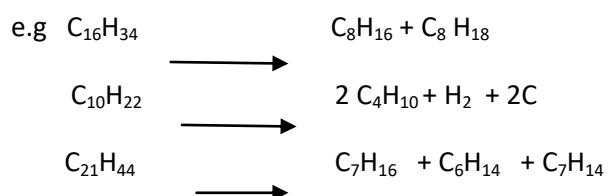| 6	**Diesel**	250-320 ^{0}C	C_{15} to C_{18}	Diesel engine fuel.
7	**Heavy oil**	320-400 ^{0}C	C_{17} to C_{30}	For making petrol by cracking
	a)Lubricating oils		C_{18} to C_{20}	As a lubricant
	b)Vaseline		C_{20} to C_{22}	In cosmetics, medicines, ointment, lubricant etc.
	c) Greases		C_{22} to C_{26}	For lubrication
	d) Wax		C_{26} to C_{30}	In candles, boot polish etc
8	**Residue** a) Asphalt b) Petroleum coke		Above C_{30}	For road making, water proofing of roofs, as fuels

Cracking of Heavy Oil

Cracking

The heavier fractions of petroleum refinery may be converted to more useful lighter fractions by a process called cracking and this involves change in molar mass.

Petrol (gasoline) and LPG have largest demand as fuels but they are not obtained as much as requirement, by the fractionation of petroleum.

Heavy oil fraction is obtained in surplus quantity during the fractionation of petroleum. Hence, the surplus heavy oil is converted into petrol and LPG by the process known as cracking.

Cracking is the process of converting bigger hydrocarbon molecules in a feed into smaller hydrocarbon molecules.

e.g $C_{16}H_{34}$ $\longrightarrow$ $C_8H_{16} + C_8 H_{18}$

$C_{10}H_{22}$ $\longrightarrow$ $2 C_4H_{10} + H_2 + 2C$

$C_{21}H_{44}$ $\longrightarrow$ $C_7H_{16} + C_6H_{14} + C_7H_{14}$
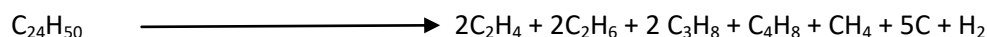
There are two methods of cracking

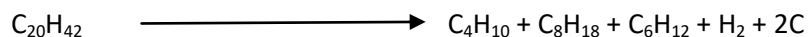1) Thermal cracking

2) Catalytic cracking

Thermal cracking

The heavy oil fraction is subjected for **high temperature and high pressure heating** (without catalyst).The hydrocarbon molecules in feed undergo thermal degradation.

In the thermal cracking, the molecules in feed, get randomly broken down to produce the smaller hydrocarbon molecules along with carbon black and H_2 e.g

Higher Temp., Press

$$C_{24}H_{50} \longrightarrow 2C_2H_4 + 2C_2H_6 + 2\ C_3H_8 + C_4H_8 + CH_4 + 5C + H_2$$

Lower Temp., Press

$$C_{20}H_{42} \longrightarrow C_4H_{10} + C_8H_{18} + C_6H_{12} + H_2 + 2C$$

Generally, thermal cracking results in the formation of **lesser yield of petrol** and more yield of gaseous products. The thermal cracking be operated in liquid phase or in vapour phase.

Point	Liquid phase thermal cracking	Vapour phase thermal cracking
Temp	Temp used for cracking is 475-530 ^{O} C	Temp used for cracking is 600-650 ^{O} C
Press	Press. operated about100 kg/cm^2	Press. operated about10-20 kg/cm^2
Evaporation	This thermal cracking method is Used when the feed oil does not evaporate easily on heating e.g heavy oil	This thermal cracking method is used only when the feed oil evaporates easily on heating e.g naphtha, diesel, lower boiling heavy oil.
Yield of petrol	Yield of petrol is better i. e 50-60%	Yield of petrol is lesser i. e about 30%
Yield of gaseous Products & Carbon	Yield of gaseous products and carbon is lesser	Yield of gaseous products (LPG) and carbon is more
Octane no	Petrol produced has lower O.N 65-70	Petrol produced has O.N greater than 70.
Time	Method requires longer time	Method requires lesser time.

Catalytic Cracking

The vaporized feed stock is made to undergo cracking by coming into contact with a solid catalyst in a finely powdered state. Cracking takes place at low temperatures and pressures. by controlling the conditions it is possible to control the nature of the end products. Catalytic cracking is essentially thermal decomposition of hydrocarbons in presence of catalysts such as a crystalline alumino-silicates (zeolites) or molecular sieves.

In petroleum refining, catalytic cracking has largely superceded thermal cracking because it produces gasoline richer in branched paraffins, cycloparaffins and aromatics.

The quantity & yield of petrol produced by catalytic cracking process is very high.

The heavy oil is heated at 425 to 500 ^{0} C in the presence of catalyst. The catalyst used is either silica + alumina or aluminium silicate $Al_2(SiO_3)_3$

The catalytic cracking involves cationic mechanism & the heavy oil molecules are cracked almost symmetrically.

e.g $C_{24}H_{50}$ $\longrightarrow$ C_8H_{18} +2C_8H_{16}

$C_{20}H_{42}$ $\longrightarrow$ 2C_7H_{14} + C_6H_{14}

Advantages of catalytic cracking are

i)   Yield of petrol is high
ii)   As the petrol produced ,contains higher proportions of cycloalkanes and branched chain alkanes, it has octane number 85 $^+$
iii)   Much lower pressure (1-5Kg/cm^2) and temperature are required for catalytic cracking.
iv)   The gaseous byproduct and carbon black produced is negligible.
v)   The catalytic cracking process can be easily controlled for desired products ie petrol or L.P.G
vi)   No external heat necessary, as the coal embedded in the catalyst burns to produce the required temperature i.e petrol or LPG.

 The catalytic cracking can be done by two methods

a) Fixed bed catalytic cracking
b) Moving bed catalytic Cracking(Fluid bed catalytic cracking)

a) Fixed bed catalytic cracking

1) The heavy oil is heated in a preheater to form vapours of cracking temperature i.e 425-450 ^{0} c.

2) Then the vapours are forced through catalytic chamber at the pressure of 1.5 Kg / cm2.The catalytic chamber is maintained at 425-450 ^{0} c. During the first pass about 40% of the feed is converted to petrol and there is also formation of 2-4% of carbon black. The carbon black gets adsorbed on the catalyst. Such catalyst stops to function after about 8 hours. It needs reactivated by burning off the deposited carbon.
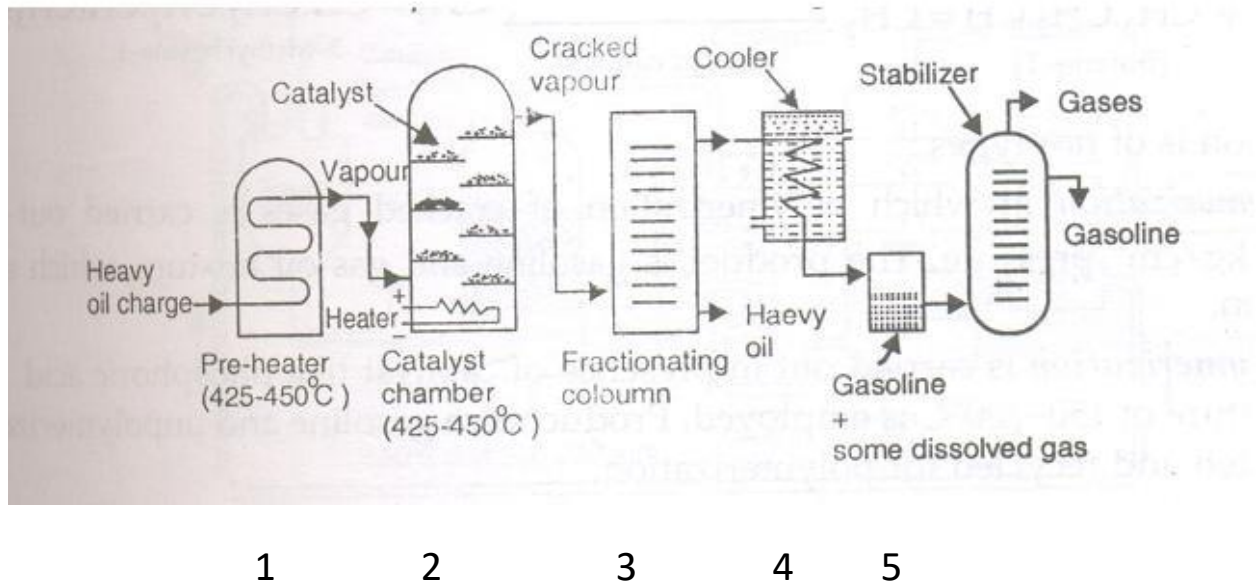
Fig Fixed bed catalytic cracking

3) The vapours from the catalytic chamber are passed to a fractionating column to condense the unconverted **heavy oil** which is recycled for further conversion.

4) The uncondensed vapours from fractionating column are cooled to get petrol.

5) This petrol is then sent to stabilizer, where gaseous products get expelled.

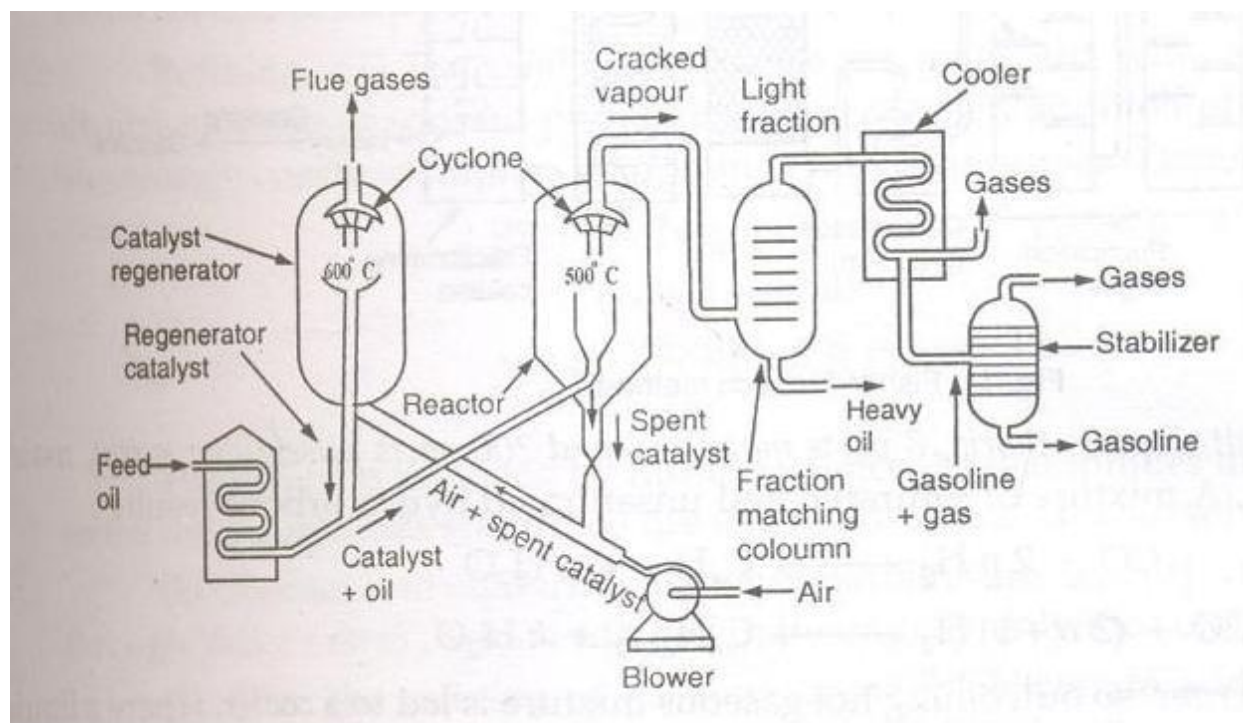## b) Moving bed catalytic cracking(Fluid bed catalytic cracking)

Principle:- In fluid bed catalytic cracking, the finely powdered catalyst is kept agitated by a gas stream of the vaporized heavy oil feed stock. Thus, the catalyst can be handled like a fluid

system and can be pumped like a liquid. This brings about a close contact between the catalyst and the reactant and results in a more efficient cracking.

Method:-

A schematic representation of the fluid bed catalytic cracking is shown in fig.

Cyclone separator   Reactor

Preheater

1   2   3

Fig :- Moving bed catalytic cracking

1) The feed oil is first preheated to form vapours .
2) These vapours along with finely powdered catalyst then pass in a reactor maintained at 450-500 ^{0} c. The catalyst used is silica alumina gel or of bauxite mixed with clay (and zineonium oxide)

3) The cracked oil vapours then passed through fractionating column where unconverted heavy oil condenses. This heavy oil is recycled for further conversion.

4) The uncondensed vapours from fractionating column then are cooled to get the gasoline.

5) The gaseous byproducts are removed from gasoline in the stabilizer.

The catalyst powder does not pass forward from the reactor but settles at its bottom due to carbon black deposition on catalyst powder particles. This spoiled catalyst is regenerated by forcing it to regenerator where the deposited carbon is burnt off. The regenerated catalyst is then passed along with feed oil vapours into the reactor.

Spent catalyst is continuously pumped from the catalyst chamber into a regeneration chamber. Hot air is blown through it to burn the carbon deposited on the catalyst surface. The regenerated catalyst is sent back to catalyst chamber. Thus the process of cracking is made continuous.

Catalyst (y type of zeolite with rare earth oxide or a zeolite) in the finely divided state is kept in the cracking chamber (reactors).it is kept in a fluid state by the upcoming feed stock vapours under pressure.Cracking takes place efficiently since there is very close contact between the catalyst and reactant.the cracked products are withdrawn from the top of the catalyst chamber and fed directly into a fractionating column for further separation.The uncracked oil is sent for a second stage of cracking.

	Catalytic cracking	Thermal cracking
1	Petrol yield is about 90%	Petrol yield is about 60%
2	O.N of petrol obtd.is 85^+	O.N of petrol obtd. is much lesser.
3	Lower temp.& press. required in operation	Higher temp & press. required for operation
4	By product gases negligible	Appreciable high quantity of gaseous byproducts obtained.
5	Process involves catalyst Initiated cationic mechanism Of cracking.	Involves free radical mechanism of cracking
6	The hydrocarbon molecules in feed are cracked systematically.	The molecules are cracked randomly

.

Gaseous Fuels

Liquefied Petroleum Gas (LPG)

LPG contains a mixture of saturated and unsaturated hydrocarbons in the C_3 and C_4 range such as

Propane (C_3H_8)   ,   n-butane (C_4H_{10})

Butylene (C_4H_8)   ,   propylene (C_3H_6)

Isobutane (C_4H_{10}).

Small quantities of Ethane (C_2H_6), Pentane (C_5H_{12}), Ethylene (C_2H_4) and Pentene (C_5H1_0) may also be present.

At room temperature LPG is in gaseous state. The gas on cooling and compression get converted to liquid and then filled in cylinder under the name "Liquefied Petroleum Gas" It is stored and transported as liquid under pressure but is used as gas.

.The pressure at which LPG becomes liquid is called its vapour pressure. It varies depending on composition and temperature.ex.220 KPascal for pure butane at 20^oC and 220 KPascal for pure propane at $55\,^o$C. It is supplied in pressurized steel botteles. It is sold as propane or butane or under the trade names such as HP gas, Bharat gas and Indane gas in our country.

Manufacture

It is obtained by 2 ways

1. The uncondensed gases from the fractionating column during refining of crude oil.

2. The thermal cracking of naptha or heavy oil fraction.

The condensed gases from refinery and the gaseous products of the thermal cracking of petroleum fraction contain mainly propane

Properties

1. LPG has C.V about 25000 Kcal/m3.

2. LPG is colourless, odourless and non toxic gas. To sense the accidental leakage of LPG from cylinder, a small amount of highly odorous organic sulphur compound is mixed in LPG. The mercapton or thioether has characteristic smell.

3. It burns with blue flame and is it is clean to use.

4. LPG is mainly Propane, Butane or a mix. of Propane and butane. Since LPG has such a simple chemical structure, it is among the cleanest of any alternative fuels.

5. The combustion of LPG produces carbon dioxide and water vapour on complete combustion. Inadequate air supply or ventilation can result in the production of carbon monoxide which can be toxic.

6. LPG vapour is denser than air; the vapour may flow along the ground and be ignited at a considerable distance from the source of leakage.

7. LPG is generally non corrosive to steel and copper alloys.

8. At room temperature LPG is in gaseous state. The gas on cooling and compression get converted to liquid and then filled in cylinder under the name "Liquefied Petroleum Gas" Its weight is approximately half that of an equivalent volume of water.

9. It is highly knocking resistant and therefore, it burns cleanly without forming any residue.

10. The B.P of LPG varies from $-44^{0}C$ to $0\,^{o}\,C$.

Applications of LPG

1. **As domestic fuel.**

As a cooking gas, LPG is safer than most fuels because neither LPG itself nor the end products that are produced by burning LPG are poisonous. Since LPG cannot burn without air, there can never be a 'flash-back' into the cylinder.

2. As a power source for **combined heat and power technologies**. (CHP)

CHP is the process of generating both electrical power and useful heat from a single fuel source. This technology has allowed LPG to be used not just as fuel for heating and cooking but also for de-centralized generation of electricity.

3. **As industrial fuel.**

It is used as industrial fuel since; it burns more cleanly than petrol or fuel-oil and is especially free of the particulates.

Other industrial applications of LPG include its use in portable blow- lamps, soldering, welding, annealing, hardening, steel cutting, etc.

4. **As motor fuel**.

When LPG is used to fuel internal combustion engines, it is often referred to as auto gas or auto propane. It is non toxic, non –corrosive and additives are not required to reduce knocking. It has high octane rating.

5. **As a feedstock**.

It is used as a feedstock for the manufacture of various chemicals and olefins by pyrolysis.

6. **Advantages of LPG**

1. High Octane rating enables it to mix better with air and to burn more completely than does gasoline, generating less carbon. With less carbon buildup, spark plugs often last longer and oil changes are needed less frequently.

2. Because LPG burns in the engine in the gaseous phase, propane results in less corrosion and engine wear than does gasoline.

3. LPG does not pollute underground water sources, because it vaporizes when released from the tank and is not water soluble.

4. Its advantage as auto gas is that it is non –toxic, corrosive and free of tetraethyl lead or any additives, and has a high octane rating.

Drawbacks/Limitations of LPG

1. It is not highly available.

2. It is not as available as petrol and diesel but can be found at few of service stations in India.

3. It has a lower energy density than petrol. (So the equivalent fuel consumption is higher)

4. The gas tank takes up a considerable amount of space in the car.

5 Burning of 100L of LPG emit about 160 kg of carbon dioxide into the atmosphere.

6. LPG is generally higher priced than other fuel alternatives such as CNG and gasoline.

7. In cold conditions, below 0° C, starting could be a problem, because of the low vapor pressure of propane at low temperature.

Natural Gas

Natural gas is mainly composed of methane and small quantities of ethane and other hydrocarbons. If lower hydrocarbons (chiefly methane and ethane) are present, the natural gas is called 'dry' or lean. If higher hydrocarbons are present along with methane, the natural gas is called "Rich" or "Wet" It is also called "marsh gas" because it majorly contains methane (Marsh gas usually seen rising from the bottom of a covered swamp or marsh as an occasional bubble, is largely methane).

The average composition of natural gas is as follows

$CH_4 = 88.5\%$

$C_2H_6 = 5.5\%$

$C_3H_8 = 3.7\%$

$C_4H_{10} = 1.8\%$

$C_{5+} = 0.5\%$

It may also contain H_2, CO and CO_2."Sour" natural gas may contain appreciable quantities of H_2S as in Lacq (France) where it is up to 15%

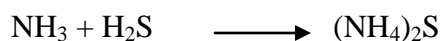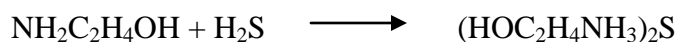The calorific value of natural gas varies from 8000 to 14000 Kcal/m^3

Natural gas is subjected to various treatments before it reaches the consumer. Wet natural gas is treated to recover the vapours of liquid hydrocarbons
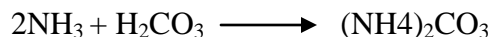
a) by condensation (pressure and cooling),

 b)by absorption in oil and

c) by adsorption on charcoal, silica or alumina gel.

The liquid so recovered is known as "casinghead gasoline"

The natural gas is processed further to remove undesirable components such as 1) water 2) grit and dust 3) H_2S 4) CO_2 and 5)N_2

 H_2S and CO_2 are removed and recovered with mono-ethanolamine ($NH_2C_2H_4OH$) or other ammonia derivatives:

$$NH_2C_2H_4OH + H_2S \longrightarrow (HOC_2H_4NH_3)_2S$$

$$NH_3 + H_2S \longrightarrow (NH_4)_2S$$

$$2NH_3 + H_2CO_3 \longrightarrow (NH4)_2CO_3$$

Natural gas is finding increasing use as a domestic and industrial fuel and as a raw material for the synthesis of methanol, formaldehyde and other chemical compounds.

Natural gas is used as a source of H_2. Ammonia used in one of the processes for extracting nickel from its ores is made by reacting N_2 (from liquid air) with natural gas. Sulfur is also removed from H2S containing natural gas

$$2H_2S + 3O_2 \longrightarrow 2SO_2 + 2H_2O$$

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$
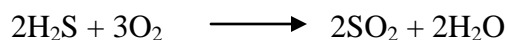
India's proved reserves of natural gas are of the order of 40Km3,most of which lie in Assam and Gujrat.

Compressed Natural Gas (CNG)

The compressed natural gas, CNG contains mainly CH_4.

CNG is obtained from processing of natural gas.

Natural gas deposits exist in nature in association with crude oil or as free gas.

Natural gas because of its low energy density has either compressed to high pressure or cooled to liquid state at about -160 ^{o} C, to store it in the vehicle to provide the necessary operating range.

Natural gas has composition $CH_4 = 70$ to 83%.

C_2 to C_4 Hydrocarbons = 10-30%

$C_4{}^+$ hydrocarbons $= 0.3$ to 3%

CO =1%

$CO_2 = 1$ to 2%

$N_2 = 0.5$ to 5%

And certain small amounts of H_2S and H_2O vapours.

Properties

- Low carbon hydroxide, hydrocarbon & sulphur emissions.
- Low energy density

- Compressed to high pressures or cooled to liquid states.

Applications:

- CNG is a substitute for gasoline or diesel fuel.
- As a domestic fuel instead of LPG.
- Used for manufacturing of fabrics, glass, steel, plastics, paints, etc.
- In power generation.
- It is used as raw material for making carbon black and hydrogen gas.
- It is used for industrial heating.
- For lighting and cooking also.

Advantages

- Economical and clean
- Cetane no 130 and hence no anti-knocking additive is required.
- Light weight with high ignition temperature.
- Emission of CO & un-burnt hydrocarbon is less.
- Lower maintenance cost.
- Does not carbonize spark plugs.
- CNG engine has long life.
- Better cold starting characteristics.
- Reduce noise from running vehicles.
- It mixes easily with air during combustion.
- It has high calorific value of about 13000 calories/liter.
- Combustion of CNG in the engine is much smooth.

Disadvantages :

- It requires large space for storage as compared to conventional fuel.
- It require additional component for storage of fuel which cost more than petrol tank.
- Lack of sufficient fuel stations throughout the country.
- The compressed gas must be maintained at very high pressure so it is stored in reasonably small volume, heavy fuel tanks, with thick walls.
- Incomplete combustion of methane leads to increased global warming because CH_4 is a green house gas.
- CNG driven vehicles have shorter operating range.
- Refueling networks for CNG are very expensive.