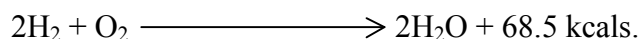
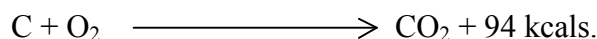


FUELS AND COMBUSTION CHEMISTRY

Classification, Characteristics of fuel, Combustion processes- Calorific value: gross and net calorific values. Solid Fuels: Coal-Classification, Analysis: Proximate and Ultimate analysis of coal and their importance, Metallurgical coke: Properties, Manufacture by Otto Hoffman process. Liquid fuels- Synthetic Petrol: Fischer-Tropsch process and Bergius Process, Knocking and anti-knocking, octane number and cetane number and their significance, Gaseous Fuels: Natural gas, synthetic gas (water gas, producer gas). Flue gas analysis – Orsat apparatus.

INTRODUCTION

Fuels are the main energy sources for industry and domestic purposes. “A fuel is a substance containing carbon as the major substituent which provides energy on combustion for industry and domestic purposes”. During the process of combustion of a fuel, the atoms of carbon, hydrogen, etc combine with oxygen with simultaneous liberation of heat. The calorific value of a fuel depends mainly on the two elements.



The combustion is the process of oxidation that provides heat energy. Every combustion is an oxidation but every oxidation is not combustion. The carbon compounds have been used for many centuries as the source of heat and energy. The main source of fuel is coal and petroleum. These are stored fuels available in earth's crust and are generally called fossil fuels because they were formed from the fossilised remains of plants and animals.

CHARACTERISTICS OF A GOOD FUEL

1. The fuel should be easily available.
2. It should be dry and should have less moisture content. Dry fuel increases its calorific value.
3. It should be cheap, easily transportable and has high calorific value.
4. It must have moderate ignition temperature and should leave less ash after combustion.
5. The combustion speed of a good fuel should be moderate.
6. It should not burn spontaneously to avoid fire hazards.
7. Its handling should be easy and should not give poisonous gases after combustion.
8. The combustion of a good fuel should not be explosive.

CLASSIFICATION OF FUELS

Classification of fuels is based on two factors.

1. Occurrence (and preparation): On the basis of occurrence, the fuels are further divided into two types.
A. Natural or Primary fuels: - These are found in nature Ex: - Wood, peat, coal, petroleum, natural gas etc.

B. Artificial or Secondary fuels: - These are prepared artificially from the primary fuels.

Ex: - charcoal, coke, kerosene, diesel, petrol, coal gas, oil gas, producer gas, blast Furnace gas etc.

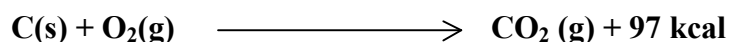
2. The second classification is based upon their state of aggregation:

a) Solid fuels b) Liquid fuels and c) Gaseous fuels.

Type of fuel	Natural or primary fuel	Artificial or secondary fuel
Solid	Wood, peat, lignite, dung, bituminous coal and anthracite coal	Charcoal, coke etc.
Liquid	Crude oil	Petrol, diesel and various other fractions of petroleum
Gaseous	Natural gas	Coal gas, oil gas, bio gas, water gas etc.

COMBUSTION

Combustion may be defined as the exothermic chemical reaction, which is accompanied by heat and light. It is the union of an element or a compound with oxygen. Example:



In common fuels it involves the burning of carbon and hydrogen in air and also to a much smaller extent of sulphur. The presence of moisture in coal is undesirable, because it causes waste of heat; moisture may be present in coal naturally or by adding i.e. moistening the coal before use. The presence of some sort of moisture in coal helps to keep the temperature of the fire bars low and prevents the formation of clinkers. The excess presence of moisture leads to heavy smoking and leads to slow start of combustion process. Optimum free moisture content is 7 to 9% when the coal has minimum density. The presence of moisture in combustion makes the combustion process successful.

The combustible substance, usually present in fuels, which enter into the combustion, are mainly C, H, S and O. But N, CO₂ and ash are incombustible matters present in the fuel. Does not take any oxygen during combustion. Substances always combine in definite proportions, which are determined by the molecular weights of the substances.

CALORIFIC VALUE

The prime property of a fuel is its capacity to supply heat. Fuels essentially consist of carbon, hydrogen, oxygen and some hydrocarbons and the heat that a particular fuel can give is due to the oxidation of carbon and hydrogen.

Normally when a combustible substance burns the total heat depends upon the quantity of fuel burnt, its nature, air supplied for combustion and certain other conditions governing the combustion. Further the heat produced is different for different fuels and is termed as its calorific value.

Calorific value of fuel may be defined as “the total quantity of heat liberated, when a unit mass (or volume) of a fuel is burnt completely”.

(OR)

“Calorific value is the amount of heat liberated by the complete combustion of a unit weight of the fuel and is usually expressed as cal gm^{-1} or kcal gm^{-1} or B.Th.U.

(OR)

The calorific value of a fuel can be defined as “the total quantity of heat liberated when a unit mass of the fuel is completely burnt in air or oxygen”.

There are different units for measuring the quantity of heat. They are:

1. Calorie	2. Kilocalorie	3. British thermal unit (B.Th.U)	4. Centigrade heat unit (C.H.U).
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1. Calorie: It is the amount of heat required to increase the temperature of 1 gram of water through one degree centigrade.

2. Kilocalorie: This is the unit of heat in the metric system, and is defined as the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade.

$$1 \text{ k.cal} = 1000 \text{ cal} \quad 1 \text{ k.cal} = 3.968 \text{ B.Th.U}$$

3. British thermal unit (B.Th.U): This is the unit of heat in English system, it is defined as “the quantity of heat required to increase the temperature of one pound of water through one degree of Fahrenheit.

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

4. Centigrade heat unit (C.H.U): It is the quantity of heat required to raise the temperature of one pound of water through one degree centigrade.

$$1 \text{ k cal} = 3.968 \text{ B.Th.U} = 2.2 \text{ C.H.U}$$

HIGHER OR GROSS CALORIFIC VALUE

It is the total amount of heat produced, when unit mass/volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature (15°C or 60°F). It is explained that all fuels contain some hydrogen and when the calorific value of hydrogen containing fuel is determined experimentally, the hydrogen is converted into steam. If the products of combustion are condensed to the room temperature, the latent heat of condensation of steam also gets included in the measured heat which is then called GCV.

LOWER OR NET CALORIFIC VALUE

It is the net heat produced, when unit mass/volume of the fuel is burnt completely and the products are permitted to escape. In actual practice of any fuel, the water vapour and moisture, etc., are not condensed and escape as such along with hot combustion gases. Hence a lesser amount of heat is available.

SOLID FUELS

The main solid fuels are wood, peat, lignite, coal and charcoal.

COAL

Coal is a fossil fuel, which occurs in layers in the earth's crust. It is formed by the partial decay of plant materials accumulated millions of years ago and further altered by the action of heat and pressure. The process of conversion of wood into coal can be represented as

Wood → Peat → Lignite → Bituminous Coal → Anthracite

- 1) Peat: Peat is brown fibrous jelly like mass.
- 2) Lignite: These are soft, brown coloured, lower rank coals
- 3) Bituminous coals: These are pitch black to dark grey coal
- 4) Anthracite: It is a class of highest rank coal

S.No	Fuel	Percentage of carbon	Calorific value (k.cal/kg)	Applications
1	Wood	50	4000 - 4500	Domestic fuel
2	Peat	50-60	4125-5400	Used if deficiency of high rank coal is prevailing
3	Lignite	60-70	6500-7100	For steam generation in thermal power plants
4	Bituminous	80-90	8000-8500	In making coal gas and Metallurgical coke
5	Anthracite	90-98	8650-8700	In households and for steam raising

Analysis of Coal

The analysis of coal is helpful in its ranking. The assessment of the quality of coal is carried out by these two types of analyses. A) Proximate analysis B) Ultimate analysis

A. Proximate analysis:

In this analysis, the percentage of carbon is indirectly determined. It is a quantitative analysis of the following parameters.

1. Moisture content
2. Volatile matter
3. Ash
4. Fixed carbon

1. Moisture Content

About 1 gram of finely powdered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105 to 110⁰ C for one hour. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in desiccators and weighed. Loss in weight is reported as moisture.

$$\text{Percentage of Moisture} = \frac{\text{Loss in weight}}{\text{Weight of coal taken}} \times 100$$

2. Volatile Matter

The dried sample taken in a crucible in and then covered with a lid and placed in an electric furnace or muffle furnace, maintained at 925 + 20C. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside desiccators and weighed again. Loss in weight is reported as volatile matter on percentage-basis.

$$\text{Percentage of Volatile Matter} = \frac{\text{Loss in weight}}{\text{Weight of coal taken}} \times 100$$

3. Ash

The residual coal sample taken in a crucible and then heated without lid in a muffle furnace at 700 + 50 C for ½ hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed. Hearing, cooling and weighing are repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis. Thus,

$$\text{Percentage of Ash} = \frac{\text{Weight of Ash left}}{\text{Weight of coal taken}} \times 100$$

4. Fixed carbon

$$\text{Percentage of fixed carbon} = 100 - \% \text{ of (Moisture + Volatile matter + ash)}$$

SIGNIFICANCE OF PROXIMATE ANALYSIS

Proximate analysis provides following valuable information's in assessing the quality of coal

1. Moisture:

Moisture is coal evaporates during the burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation. Therefore, moisture lowers the effective calorific value of coal. Moreover over, it quenches the fire in the furnace, hence, lesser, the moisture content, better the quality of coal as a fuel. However, presence of moisture, up to 10%, produces a more uniform fuel-bed and less of “fly-ash”.

2. Volatile matter:

A high volatile matter content means that a high proportion of fuel will distil over as gas or vapour, a large proportion of which escapes un-burnt, So, higher volatile content in coal is undesirable. A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Hence, lesser the volatile matter, better the rank of the coal.

3. Ash

Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Also, it often causes trouble during firing by forming clinkers, which block the interspaces of the grate, on which coal is being burnt. This in-turn causes obstruction to air supply; thereby the burning of coal becomes irregular. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal. The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism.

4. Fixed carbon

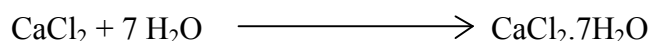
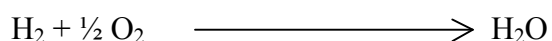
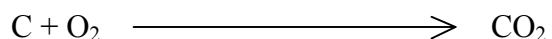
Higher the percentage of fixed carbon, greater is its calorific and better the quality coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. This also represents the quantity of carbon that can be burnt by a primary current of air drawn through the hot bed of a fuel. Hence, high percentage of fixed carbon is desirable. The percentage of fixed carbon helps in designing the furnace and the shape of the fire-box, because it is the fixed carbon that burns in the solid state.

B. Ultimate analysis

This is the elemental analysis and often called as qualitative analysis of coal. This analysis involves the determination of carbon and hydrogen, nitrogen, sulphur and oxygen.

1. Carbon and Hydrogen

About 1 to 2 gram of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO_2 and H_2O respectively. The gaseous products of combustion are absorbed respectively in KOH and CaCl_2 tubes of known weights. The increase in weights of these are then determined.



$$\text{Percentage of C} = \frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{Weight of Coal sample taken} \times 44}$$

$$\text{Percentage of H} = \frac{\text{Increase in weight of CaCl}_2 \text{ tube} \times 2 \times 100}{\text{Weight of Coal sample taken} \times 18}$$

2. Nitrogen

About 1 gram of accurately weighed powdered coal is heated with concentrated H_2SO_4 along with K_2SO_4 (catalyst) in a long-necked Kjeldahl's flask. After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as follows

$$\text{Percentage of N} = \frac{\text{Volume acid} \times \text{Normality of acid} \times 1.4}{\text{Weight of coal taken}}$$

3. Sulphur

Sulphur is determined from the washings obtained from the known mass of coal, used in bomb calorimeter for determination of a calorific value. During this determination, S is converted into Sulphate. The washings are treated with Barium chloride solution, when Barium sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

$$\text{Percentage of S} = \frac{\text{Weight of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{Weight of coal taken} \times 233}$$

4. Ash

The residual coal taken in the crucible and then heated without lid in a muffle furnace at $700 \pm 50^\circ\text{C}$ for $\frac{1}{2}$ hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed. Heating, cooling and weighing are repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis.

Thus,

$$\text{Percentage of Ash} = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}}$$

5. Oxygen

It is determined indirectly by deducting the combined percentage of carbon, hydrogen, nitrogen, sulphur and ash from 100.

$$\text{Percentage of Oxygen} = 100 - \text{percentage of (C + H + S + N + Ash)}$$

SIGNIFICANCE OF ULTIMATE ANALYSIS

1. Carbon and Hydrogen

Greater the percentage of carbon and hydrogen better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile matter and hence, it affects the use to which the coal is put.

2. Nitrogen

Nitrogen has no calorific value and hence, its presence in coal is undesirable. Thus, a good quality coal should have very little Nitrogen content.

3. Sulphur

Sulphur, although contributes to the heating value of coal, yet on combustion produces acids like SO_2 , SO_3 , which have harmful effects of corroding the equipments and also cause atmospheric pollution. Sulphur is, usually, present to the extent of 0.5 to 0.3% and derived from ores like iron, pyrites, gypsum, etc., mines along with the coal. Presence of sulphur is highly undesirable in coal to be used for making coke for iron industry. Since it is transferred to the iron metal and badly affects the quality and properties of steel. Moreover, oxides of sulphur pollute the atmosphere and leads to corrosion.

4. Ash

Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal. The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism.

5. Oxygen

Oxygen content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value, and low coking power. Moreover, oxygen is a combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about 1.7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen.

Liquid Fuels

Liquid fuels are the important commercial and domestic fuels used these days. Most of these fuels are obtained from the naturally occurring petroleum or crude oil.

Primary Petroleum

Petroleum or crude oil is a dark greenish brown, viscous oil found deep in the earth crust. Crude oil is a source of many liquid fuels that are in current use. The composition of crude petroleum approximately is C = 80-85%, H= 10-14% S= 0.1-3.5% and N=0.1-0.5%.

Refining of Petroleum

Crude oil obtained from the mine is not fit to be marked. It contains a lot of soluble and insoluble impurities which must be removed. Previously the purification of crude oil is done by simple fractional distillation. Further treatment of the products is done by refining. Refining can be defined as the process by which petroleum is made free of impurities, division of petroleum into different fractions having different boiling points and their further treatment to impart specific properties.

Refining of petroleum is done in different stages

- 1) Removal of solid impurities: The crude oil is a mixture of solid, liquid and gaseous substances. This is allowed to stand undisturbed for some time, when the heavy solid particles settle down and gases evaporate. The supernatant liquid is then centrifuged where in the solids get removed.
- 2) Removal of water (Cottrell's process): The crude oil obtained from the earth's crust is in the form of stable emulsion of oil and brine. This mixture when passed between two highly charged electrodes will destroy the emulsion films and the colloidal water droplets coalesce into bigger drops and get separated out from the oil.
- 3) Removal of harmful impurities: In order to remove sulphur compounds in the crude oil. It is treated with copper oxide. The sulphur compounds get converted to insoluble copper sulphide, which can be removed by filtration. Substances like NaCl and MgCl₂ if present will corrode the refining equipment and result in scale formation. These can be removed by techniques like electrical desalting and dehydration.
- 4) Fractional distillation: Heating of crude oil around 400°C in an iron retort, produces hot vapor which is allowed to pass through fractionating column. It is a tall cylindrical tower containing a number of horizontal stainless trays at short distances and is provided with small chimney covered with loose cap. As the vapors go up they get cooled gradually and fractional condensation takes place. Higher boiling fraction condenses first later the lower boiling fractions.

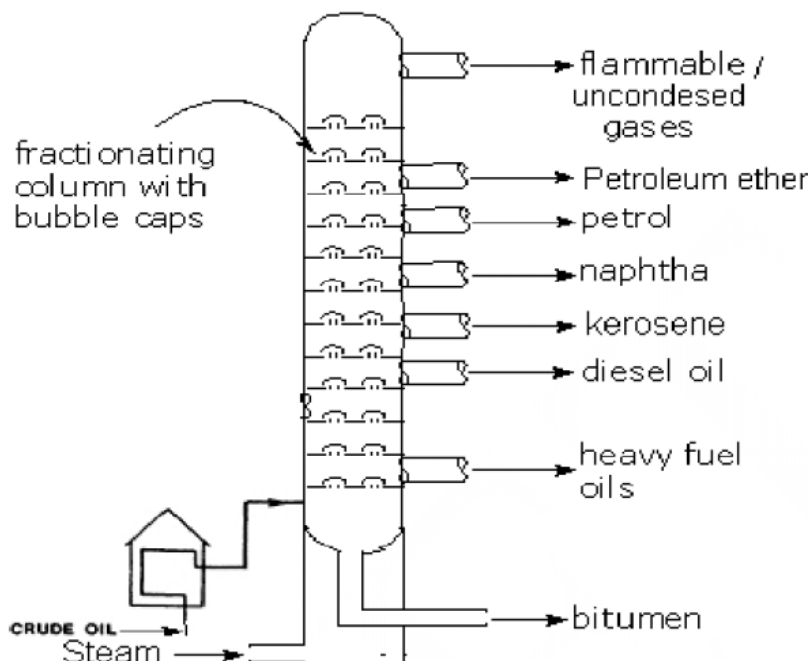
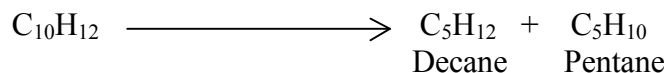


Fig. Refining of Petroleum

CRACKING

Decomposition of larger hydrocarbon molecules to smaller molecules is cracking.



Cracking is mainly two types

A. Thermal Cracking and B. Catalytic Cracking

A. Thermal cracking

If the cracking takes place at high temperature then it is thermal cracking. It may take place by two ways. They are i) Liquid-phase Thermal cracking and ii) Vapour-phase Thermal cracking

The liquid phase cracking takes place at 475⁰C to 530⁰C at a pressure 100 kg/cm². While the vapor phase cracking occurs at 600 to 650⁰C at a low pressure of 10 to 20 kg/cm²

B. Catalytic cracking

If the cracking takes place due to the presence of catalyst than it is named as catalytic cracking. Catalytic cracking may be fixed bed type or moving bed type.

i) Fixed bed catalytic cracking:

The oil vapors are heated in a pre-heater to cracking temperatures (420 – 450⁰C) and then forced through a catalytic chamber maintained at 425 – 450⁰C and 1.5 kg/cm² pressure. During their passage through the tower, about 40% of the charge is converted into gasoline and about 2 – 4% carbon is formed. The latter adsorbed on the catalyst bed.

The vapour produced is then passed through a fractionating column, where heavy oil fractions condense. The vapors are then led through a cooler, where some of the gases are condensed along – with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a ‘stabilizer’, where the dissolved gases are removed and pure gasoline is obtained. The catalyst, after 8 to 10 hours, stops functioning, due to the deposition of black layer of carbon, formed during cracking. This is re-activated by burning off the deposited carbon. During the re-activated interval, the vapors are diverted through another catalyst chamber.

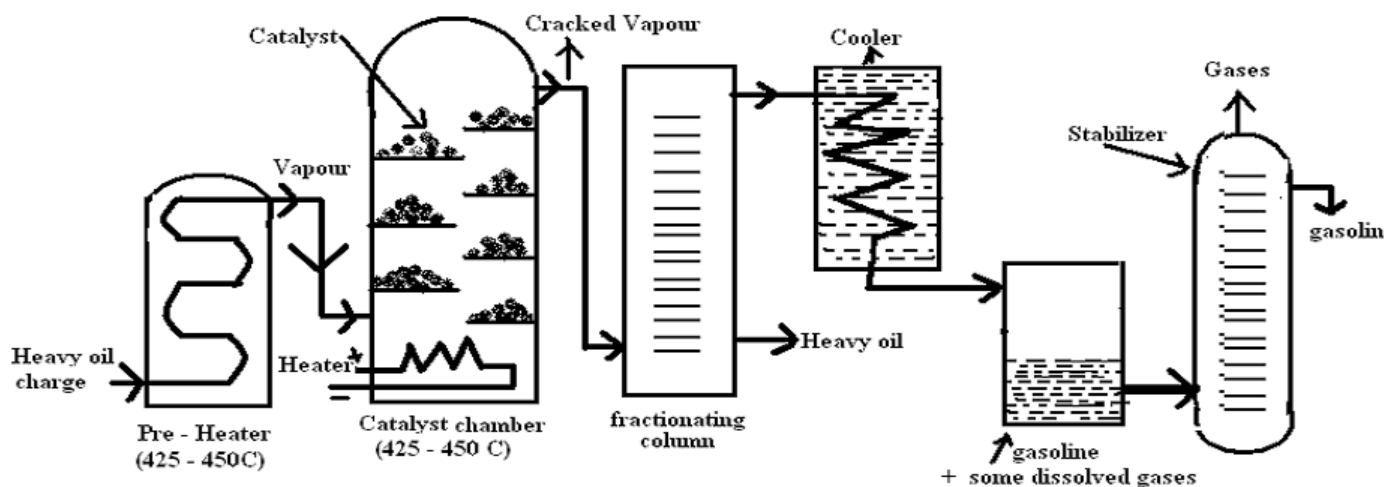


Fig. Fixed-Bed Catalytic Cracking

The catalyst, after 8 to 10 hours, stops functioning, due to the deposition of black layer of carbon, formed during cracking. This is re-activated by burning off the deposited carbon. During the re-activated interval, the vapors are diverted through another catalyst chamber.

KNOCKING

Premature and instantaneous ignition of petrol – air (fuel-air) mixture in a petrol engine, leading to production of an explosive violence is known as knocking.

In an internal combustion engine, a mixture of gasoline vapor and air is used as a fuel. After the initiation of the combustion reaction, by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture; thereby the expanding gas drives the piston down the cylinder.

The ratio of the gaseous volume in the cylinder at the end of the suction-stroke to the volume at the end of compression ratio. The efficiency of an internal combustion engine increases with the compression ratio, which is dependent on the nature of the constituents present in the gasoline used. In certain circumstances (due to the presence of some constituents in the gasoline used), the rate of oxidation becomes so great that the last

portion of the fuel air mixture gets ignited instantaneously, producing an explosive violence, known as knocking. The knocking results in loss of efficiency.

Some of the effects of knocking or detonation are 1) Carbon deposits on liners and combustion chamber 2) Mechanical damage 3) Increase in heat transfer 4) Noise and roughness 5) Decrease in power output and efficiency	The knocking can be controlled or even stopped by the following methods 1) Increasing engine r.p.m; Retarding spark 2) Reducing pressure in the inlet manifold by throttling 3) Making the ratio too lean or rich, preferably latter 4) Water injection increases the delay period as well as reduces the flame temperature. Use of high octane fuel can eliminates detonation. High octane fuels are obtained by adding additives known as dopes like tetraethyl lead, benzol, xylene to petrol.
Chemical structure and knocking: The tendency of fuel constituents to knock in the following order. Straight chain paraffins > Branched chain paraffins (i.e., iso paraffins) > Olefins > Cyclo paraffins (i.e., naphthalenes) > aromatics. Thus, olefins of the same carbon chain length possess better anti knock properties than the corresponding paraffin and so on.	

OCTANE NUMBER

The knocking characteristic of a fuel can be easily expressed by octane number. The antiknocking value of n-heptane is taken as 0 (zero) because n-heptane knocks very badly. Whereas the anti-knock value of iso-octane is approximately taken as 100 because iso-octane knocks very little.

Actually the octane number is the percentage of iso-octane in a mixture of n-heptane in order to matches the knocking characteristics of the fuel. In this way, an “80-octane” fuel is one which has the same combustion characteristics as an 80:20 mixture in iso-octane and n-heptanes.

Gasoline with octane rating as high as 135 are used for aviation purposes. The octane number of poor fuels can be raised by the addition of extremely poisonous materials as tetra ethylene lead $(C_2H_4)_4Pb$ and diethyl-telluride $(C_2H_4)_2Te$

Octane rating: It has been found that n-heptane, Knocks very badly and hence, its anti-knock value has arbitrarily been given zero. On the other hand, isooctane (2: 2: 4 – trimethyl pentane). It gives very little knocking, so its anti-knock value has been given as ‘100’. Thus, octane number (or rating) of a gasoline (or any other internal combustion engine fuel) is the percentage of isooctane in a mixture of isooctane and n-heptane, which matches the fuel under test in knocking characteristics. In this way, an “80-octane” fuel is one which has

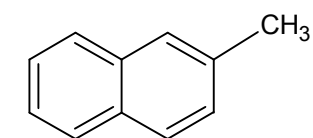
the same combustion characteristics as an 80:20 mixture of isooctane and n-heptane.

Advantages: Usually petrol with low octane number is not good quality petrol. It often knocks (i.e., produces huge noise due to improper combustion). As a result of knocking, petrol is wasted; the energy produced cannot be used in a proper way. When tetra ethyl lead is added, it prevents knocking, there by saves money and energy. Usually 1 to 1.5 ml of TEL is added per 1lit of petrol.

CETANE NUMBER

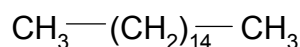
In a diesel engine, the fuel is exploded not by a spark but by the application of heat and pressure. Diesel engine fuels consist of longer chain hydrocarbons than internal combustion engine fuels. In other words, hydrocarbon molecules in a diesel fuel should be as far as possible the straight chain ones, with a minimum admixture of aromatics and side chain hydrocarbon molecules.

The suitability of a diesel fuel is determined by its cetane value which is the percentage of hexadecane in a mixture of hexadecane and 2-methyl naphthalene, which has the same ignition characteristics as the diesel fuel in question.



2-methylnaphthalene

Cetane Number = 0



n-hexadecane

Cetane Number = 100

The cetane number of a diesel fuel can be raised by the addition of small quantity of certain pre-ignition dopes like ethyl nitrite, isoamyl nitrite, acetone peroxide. An oil of high octane number has a low cetane number and vice-versa. Consequently, petroleum crude gives petrol of high octane number and diesel of low cetane number.

SYNTHESIS OF GASOLINE

The gasoline obtained from the fractional distillation of crude petroleum oil is not enough to meet the requirement of the present community due to vast increase of automobiles. Hence an alternate source need of finding out to manufacture synthetic petrol.

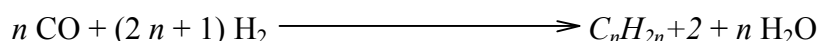
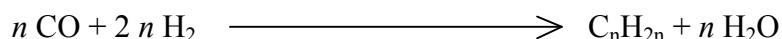
Synthetic petrol can be manufactured by the process of hydrogenation of coal. The preparation of liquid fuels from solid coal is called hydrogenation of coal.

Gasoline is synthesised by the following methods.

1. Fischer- Tropsch process.
2. Bergius process.

1. Fischer- Tropsch process

In this process, coal is first converted into coke. Then water gas is produced by the action of steam over red hot coke. It is mixed with hydrogen and the mixture is compressed to 5-25 atmospheres. The compressed gases are then led through a converter which is maintained at a temperature of 200-300°C. The converter is provided with a suitable catalyst consisting of a mixture of 100 parts cobalt, 5 parts thoria, 8 parts magnesia and 200 parts kieselguhr. A mixture of saturated and unsaturated hydrocarbons occurs as a result of polymerisation.



The reactions are strongly exothermic. Hence, the hot out coming gaseous mixture is led to a cooler where a liquid resembling crude oil is obtained. The crude oil thus obtained is then fractionated to yield gasoline and high boiling heavy oil. The heavy oil is used for cracking to get more gasoline

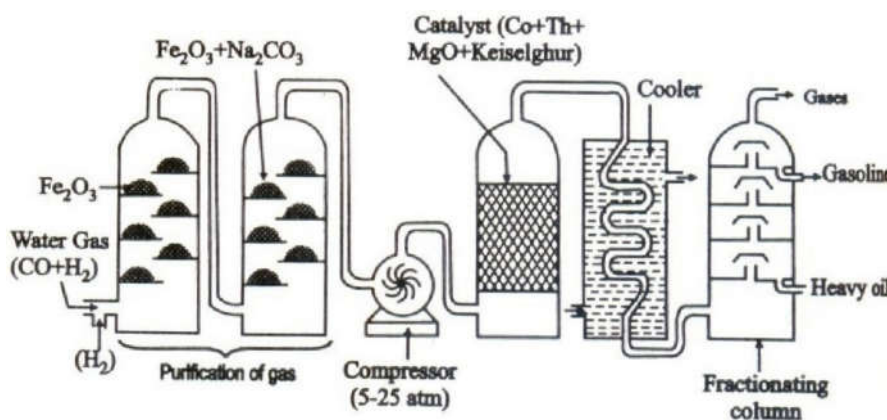


Fig: Fischer- Tropsch process

2. Bergius process

This method was developed by Bergius in Germany during the First World War. The low ash coal is *finely powdered* and made into a *paste* with *heavy oil* and then a *catalyst* (composed of tin or nickel oleate) is incorporated. The whole is heated with hydrogen at 450°C and under a pressure 200-250 atm for about 1.5 hours, during which hydrogen combines with coal to form saturated hydrocarbons, which decompose at prevailing high temperature and pressure to yield low-boiling liquid hydrocarbons.

The issuing gases (from the reaction vessel) are led to condenser, where a liquid resembling crude oil is obtained, which is then fractionated to get: (i) gasoline, (ii) middle oil, and (iii) heavy oil. The latter is used again for making paste with fresh coal dust. The middle oil is hydrogenated in vapour-phase in presence of a solid catalyst to yields more gasoline. The yields of gasoline in about 60% of the coal dust used.

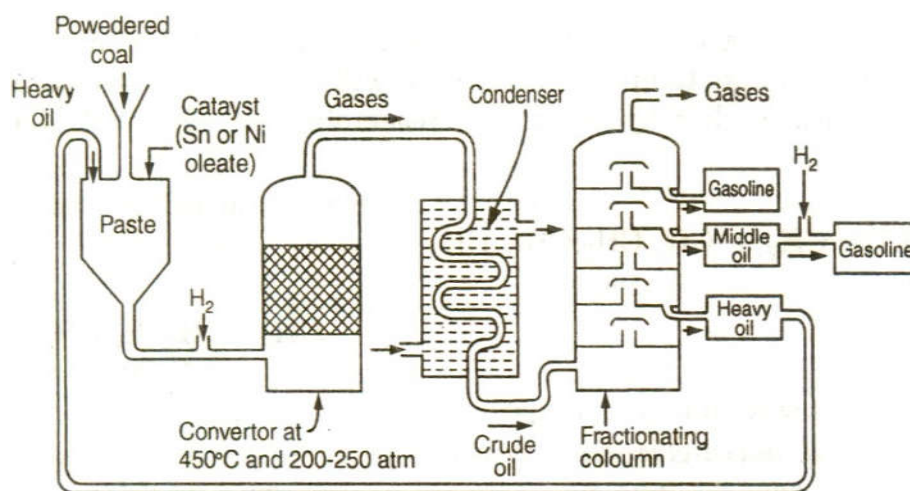


Fig: Bergius process

METALLURGICAL COKE

When bituminous coal (coal containing about 90 % carbon) is heated strongly in absence of air, the volatile matter escapes out and a white, lustrous, dense, strong, porous and coherent mass is left which is called metallurgical coke.

Good coke for metallurgy should possess the following *requisites*:

(1) Purity

It should have moisture, ash, sulphur and phosphorus contents as low as possible. A low percentage of moisture helps in keeping down the heating expenses. Excess of ash hinders the heating and also helps in slag formation, which is not desirable in fuels. According to Dr. Mott, 2% of excess coke is required for the removal of 1 % ash. Presence of S and P gives on burning, undesirable products like SO₂, P₂O₃ and P₂O₅, which adversely affect the quality of the metal being produced. Moreover, presence of sulphur makes the coke brittle.

(2) Porosity

Coal should be porous, so that oxygen can easily come in contact with the carbon of coke, thereby helping in complete combustion at a high rate.

(3) Strength

The coke should be quite compact, hard, strong to withstand dropping abrasion as well as the pressure of the over-burden (ore + fuel + flux) in the furnaces. It would be useless to employ weak coke in blast furnaces, as the weight of ore, etc., would crush the coke to breeze and thus prevent the essential passage of gases up the furnace.

(4) Size

The size of metallurgical coke should be neither too big nor too small. In case the size is too big, the uniformity of heating is never maintained, but on the other hand, if the coke size is too small, choking will result.

(5) Cost: Coke should be cheap and easily available near the site of the metallurgical plant, so that the transportation cost is low.

(6) Combustibility

Coke should burn easily. The combustibility of coke depends upon the nature of the coal, carbonization temperature and reaction temperature. Cokes obtained from strongly coking coals are not as combustible as those derived from weakly caking and non-caking coals. At a given temperature, cokes obtained by high-temperature carbonization process are less combustible compared to those obtained by low-temperature carbonization. However, at high combustion temperatures (800° - 900°C), all cokes appears to be equally reactive. At about 1,000°C, it appears that the rate of combustion depends only on the rate of oxygen/air supply.

(7) Calorific value: The calorific value of coke should be high.

(8) Low ash, S and P contents to avoid the incorporation of these in the metal to be extracted.

(9) Reactivity to steam: Reactivity towards steam increases with the reaction temperature and varies inversely with carbonizing temperature at which the coke was produces. Moreover, coke derived from non-caking coals are more reactive to steam than those derived from taking coals.

Types of carbonization of coal

(1) Low-temperature carbonization:

In this process, the heating of coal is carried out at 500 -700°C. The yield of coke is about 75-80% and it contains about 5-15% volatile matter. *It is not mechanically strong, so it cannot be used as a metallurgical coke.* However, it burns easily giving practically a smokeless, hot and radiant fire. Hence, it is suitable for domestic purposes. The byproduct gas produced (about 130-150 m³/tonne) by this process is richer in heating value (about 6,500-9,500 kcal/m³) and is, therefore, a more valuable gaseous fuel.

(2) High-temperature carbonization:

High-temperature carbonization is carried out at 900 - 1,200°C with the object of producing coke of the right porosity, hardness, purity, strength, etc., so that it can be used in metallurgy. Nearly all the volatile matter of coal is driven off and the yield of coke is about 65-75%, containing only 1- 3% volatile matter. The by-product gas produced is high in volume (about 300-390 m³/tonne), but its calorific value is low (about 5,400 6,000 kcal/m³).

MANUFACTURE OF METALLURGICAL COKE

OTTO HOFFMAN'S BY-PRODUCT OVEN METHOD:

In order to (i) save the fuel for heating purpose and (ii) recover valuable by-products like coal gas, ammonia, benzol oil, tar etc. Otto Hoffmann developed a modern by-product coke oven. Here, the heating is done externally by a portion of coal gas produced during the process itself. It also utilizes the waste flue gases for heating the checker work bricks.

The oven consists of a number of narrow silica chambers, each about 10-12 m long, 3-4 m tall and 0.4-0.45 m wide, erected side by side with vertical flues between them to form a sort of battery. Each chamber has a hole at the top to introduce the charge, a gas off take and a refractory lined cast iron door at each end for coke discharge. The oven works on heat regenerative principle i.e. the waste gas produced during carbonization is utilized for heating. The ovens are charged from the top and closed to restrict the entry of air.

Finely powdered, crushed coal is introduced through the charging hole at the top of the chambers which are then tightly closed at both ends to cut off the supply of air. The ovens are heated to 1200° deg C by burning producer gas. The air required for the combustion of the fuel is preheated in regenerators flanking the retorts, while the flue gases leave their acquired heat to one generator; the other generator is used for preheating the incoming air. The cycle goes on and the heating is continued until all the volatile matter has escaped. It takes nearly 18 hours for carbonization of a charge.

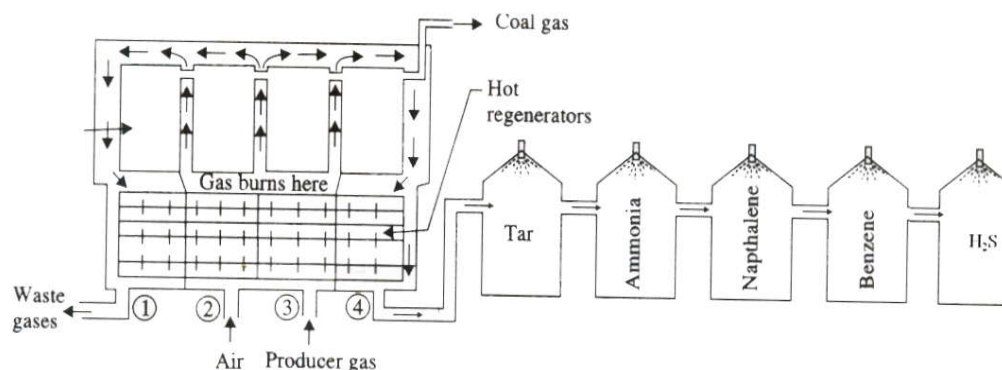


Fig: Manufacture of Metallurgical Coke - Otto Hoffman's by-product oven method

The heating of air-alone is required if the fuel gas is coal gas which has a high calorific value. If the fuel is producer gas or blast furnace gas, both air and fuel need to be preheated as they have low calorific value. When the carbonization is over, the red hot coke is pushed out into truck by a massive ram. It is then quenched by spraying water (wet quenching). Alternatively, the red hot coke may be placed in a chamber and cooled by sending in inert gases from boilers. The inert gases are then circulated to boilers where they generate steam. This method is known as dry quenching. The dry quenched coke is cleaner, drier and stronger and contains lesser dust than the wet quenched. The yield is about 70 %.

Recovery of by-products:

The gas coming out of the retort is known as coke oven gas. This consists of tar, ammonia, moisture, aromatic hydrocarbons (naphthalene, benzene), H_2S etc. It can be used as a fuel after removing coal tar and ammonia.

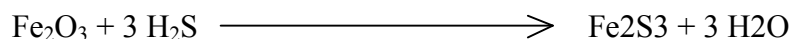
i) Recovery of tar: The coke oven gas is first passed through a tower in which liquid ammonia is sprayed. Tar and dust get collected in a tank below, which is heated by a steam coil to recover back the ammonia sprayed.

ii) Recovery of ammonia: The coke oven gas is passed through another tower in which water is sprayed. Gaseous ammonia goes into solution as NH_4OH .

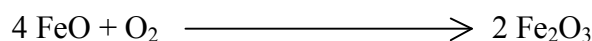
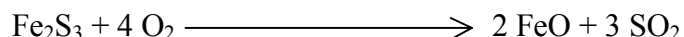
iii) Recovery of naphthalene: After recovering ammonia, the remaining gases are led through another tower where water is sprayed at low temperature when naphthalene gets condensed.

iv) Recovery of benzene: The resultant gas from the previous step is sprayed with petroleum whereby benzene and its homologues can be recovered.

v) Recovery of H_2S : The gases are then passed through a purifier, packed with moist Fe_2O_3 . Hydrogen sulphide is retained here.



When all the Fe_2O_3 is converted into Fe_2S_3 , the purifier on exposure to the atmosphere, regenerates Fe_2O_3 in the following manner.



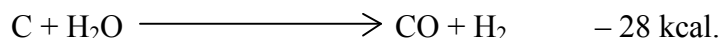
GASEOUS FUELS

WATER GAS:

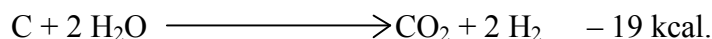
It is essentially a mixture of CO and H_2 . Its calorific value is 2800 kcal/m³. The average composition of water gas is H_2 (51 %); CO (41 %); N_2 (4 %); CO_2 (4 %).

Manufacture:

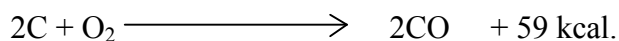
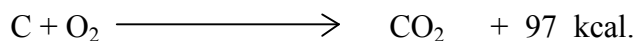
A water gas generator is a steel cylindrical vessel. At the top, it is provided with a hopper for adding coke. Water gas outlet is provided near the top. At the bottom, it is provided with an arrangement of taking out ash formed. Water gas is obtained by the action of steam on a bed of coal heated to 1000 °C.



Since the above reaction is endothermic, the coal cools down after a few minutes and the reaction proceeds in a different way to form CO_2 and H_2 , instead of water gas ($\text{CO} + \text{H}_2$).



In order to avoid the above undesirable reaction, the blow of air replaces the blow of steam. The following reactions now occur.



Due to exothermic reactions, the temperature of the bed rises and when the temperature increases to 1000 C, air entry is stopped and steam is again passed. Thus, steam and air are blown alternatively. Therefore, the manufacture of water gas is intermittent.

Uses: Water gas is used

- 1) As a source of hydrogen gas
- 2) In the manufacture of NH_3 by Haber's process.
- 3) As an illuminating gas
- 4) As a fuel gas
- 5) For welding purposes

PRODUCER GAS:

Producer gas is essentially a mixture of combustible gases (CO and H_2) associated with larger percentage of non combustible gases (N_2 and CO_2). The calorific value is only 1800 k cal/m^3 . The average composition of producer gas is 50 % N_2 ; 30 % CO ; 10 % H_2 and rest CO_2 and CH_4 .

Manufacture:

The reactor (furnace used for the manufacture of producer gas is known as producer. It consists of large airtight mild steel cylindrical towers lined inside with refractory bricks. At the bottom, it is provided with pipe for blowing air and an arrangement for removing air. Coal is added through a hopper at the top and producer gas comes out from an exit near the top.

The formation of producer gas involves the

(a) Combustion or oxidation zone:

When a mixture of air and little steam is passed through a bed of red hot coal, carbon (of the coal) combines with oxygen (of the air) in the lower part of the furnace to form CO_2 .

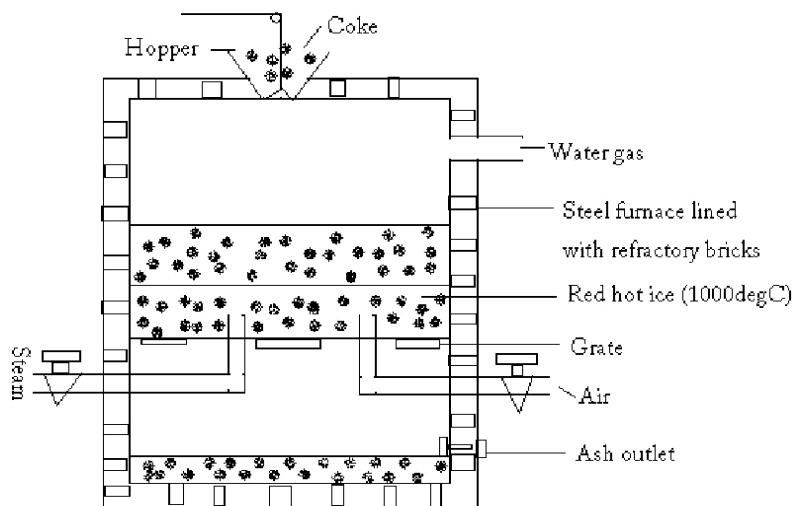
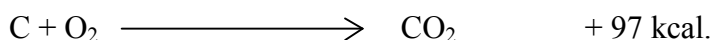


Fig: Manufacture of water gas

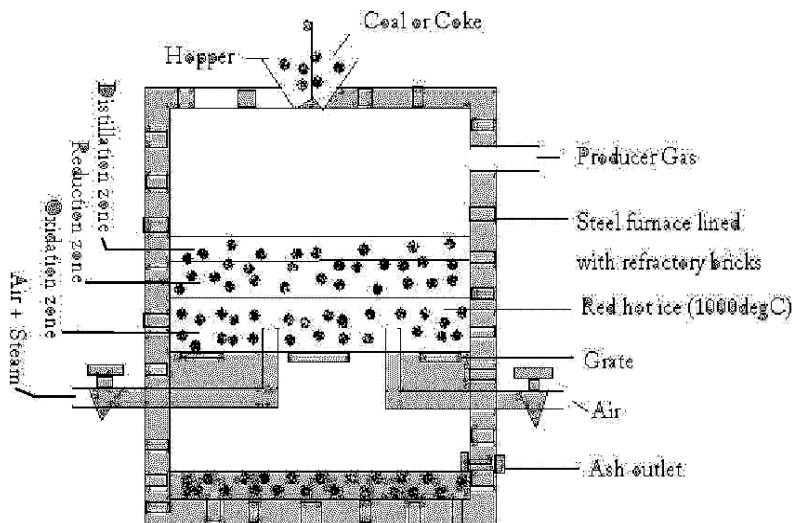
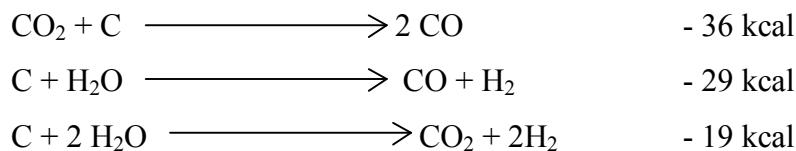


Fig: Manufacture of Producer gas

(b) Reduction zone:

Here, carbon dioxide and steam combines with the red hot coke and liberates free hydrogen and carbon monoxide.



Nitrogen of the air remain unaffected throughout the process. Thus, a mixture of CO and N₂ with traces of CO₂ and hydrocarbons comes out through the exit at the upper side of the producer.

Producer gas is a poisonous gas; insoluble in water and heavier than air.

Uses: 1) It is a cheap, clean and easily producible gas and is used for heating open hearth furnaces (in steel and glass manufacture); muffle furnaces, retorts etc., 2) As a reducing agent in metallurgical operations.

COMPRESSED NATURAL GAS (CNG)

CNG is natural gas compressed to a high pressure of about 1000 atmospheres. A steel cylinder containing 15 kg of CNG contains about 2 x 10⁴ L or 20 m³ of natural gas at 1 atmospheric pressure. It is derived from natural gas and the main constituent of CNG is methane.

Properties:

- 1) CNG is comparatively much less pollution causing fuel as it produces less CO, ozone and hydrocarbons during combustion.
- 2) During its combustion, no sulphur and nitrogen gases are evolved.
- 3) No carbon particles are ejected during combustion.
- 4) It is less expensive than petrol and diesel.
- 5) The ignition temperature of CNG is 550 °C.
- 6) CNG is a better fuel than petrol/diesel for automobiles.
- 7) CNG requires more air for ignition.

Uses:

As CNG is the cheapest, cleanest and least environmentally impacting alternative fuel.

In Delhi, it is mandatory for all buses, taxis and auto to use CNG as a fuel.

LIQUIFIED PETROLEUM GAS (LPG)

LPG or bottled gas or refinery gas is obtained as a by-product during the cracking of heavy oils or from natural gas. LPG is dehydrated, desulphurised and traces of odorous organic sulphides (mercaptans) are added to give warning of gas leak.

LPG is supplied under pressure in containers under the trade name like Indane, Bharat gas, etc. Its calorific value is about 27,800 kcal/m³. It consists of hydrocarbons of such volatility that they can exist as gas under atmospheric pressure, but can be readily liquefied under pressure. The main constituents of LPG are n-butane, isobutene, butylenes and propane, with little or no propylene and ethane.

Uses: Use as a domestic fuel and industrial fuel. Nowadays used as motor fuel.

FLUE GAS ANALYSIS – ORSAT’S APPARATUS

The mixture of gases like SO₂, CO₂, O₂, CO etc. coming out from the combustion chamber is called flue gas.

Importance of Flue Gas Analysis:

- 1) The analysis gives the idea of whether a combustion process is complete or not.
- 2) The C and H present in a fuel undergo combustion forming CO₂ and H₂O respectively. Any N present is not at all involved in the combustion. ie., the products of combustion are CO₂, H₂O and N₂.
- 3) If analysis of a flue gas indicates the presence of CO; it is suggestive of incomplete combustion. (wastage of heat is inferred)
- 4) If there is considerable amount of oxygen, it shows that there is excess supply of O₂ although combustion would have been complete.

Analysis:

The flue gas analysis is carried out by using Orsat’s apparatus. The analysis of flue gas generally deals with the determination of CO₂, O₂ and CO by absorbing them in the respective solution of KOH, alkaline pyrogallol and ammonium cuprous chloride.

Description of Orsat’s apparatus:

Orsat’s apparatus consists of a horizontal tube having 3 way stopcock at one end and a water jacketed measuring burette at the other end. The horizontal tube is connected to three different absorption bulbs for the absorption of CO₂, O₂ and CO respectively. The lower end of the burette is connected to the leveling bottle by means of rubber tube.

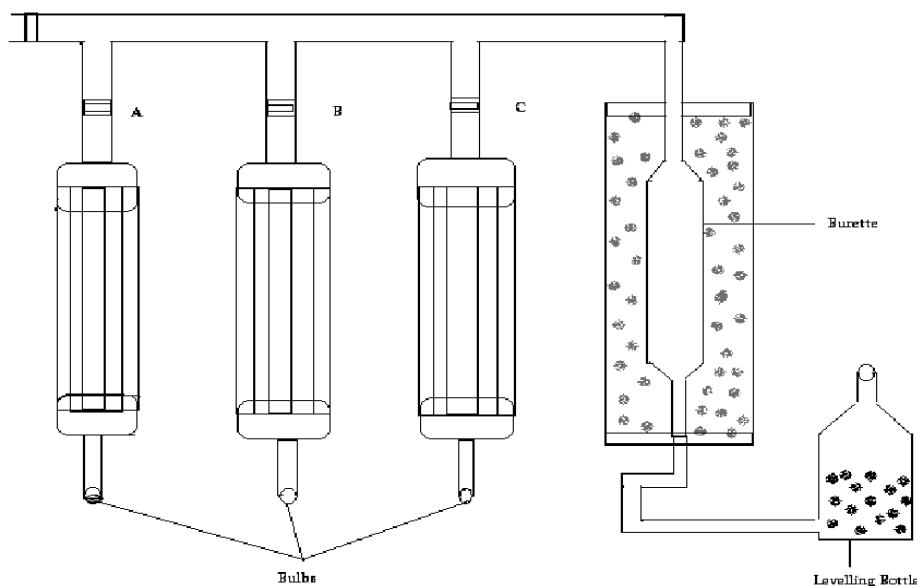


Fig - Flue Gas Analysis – Orsat’s Apparatus

The level of water in the leveling bottle (water reservoir) can be raised or lowered by raising or lowering the water reservoir. By changing the level of water, the flue gas can be moved into various parts of the apparatus during analysis.

It is essential to follow the order of absorbing the gases- CO_2 first; O_2 second and CO last.

This is because the absorbent used for O_2 (ie., alkaline pyrogallol) can also absorb some amount of CO_2 and the percentage of CO_2 left would be less.

a) Absorption of CO_2

Flue gas is passed into the bulb A via its stopcock by raising the water reservoir. CO_2 present in the flue gas is absorbed by KOH (usually 250 g KOH in 500 mL distilled water). The gas is again sent to the burette and then again sent to bulb A. This process is repeated several times, by raising or lowering of water reservoir so as to ensure complete absorption of CO_2 in KOH . Now, the stopcock of bulb A is closed. The volume of residual gases in the burette is taken by equalizing the water level both in the burette and in the water reservoir. The difference between original volume and the volume of the gases after CO_2 absorption gives the volume of CO_2 absorbed.

b) Absorption of O_2

Stopcock of bulb A is closed and bulb B is opened. Oxygen present in the flue gas is absorbed by alkaline pyrogallol (25 g pyrogallol + 200 g KOH in 500 mL distilled water). The absorption process is same as in bulb A.

c) Absorption of CO

Now the stopcock of bulb B is closed and stopcock of bulb C is opened. Carbon monoxide present in the flue gas is absorbed by ammoniacal cuprous chloride (100 g Cu_2Cl_2 + 125 mL liquid NH_3 + 375 mL water). Here also absorption process is same as in bulb A.

Since the total volume of the gas taken for analysis is 100 mL, the volume of the constituents are their percentage.

The residual gas after the above three determinations is taken as nitrogen.

Further, as the content of CO in the flue gas would be very low, it should be measured quite carefully.