*Unit*IV

FUELS AND COMBUSTION

Fuels: Introduction – Classification of fuels – Coal - Analysis of coal (proximate and ultimate) – Carbonization – Manufacture of metallurgical coke (Otto Hoffmann method) – Petroleum – Manufacture of synthetic petrol (Bergius process) – knocking – Octane Number – Diesel Oil – Cetane Number – Natural Gas – Compressed Natural Gas (CNG) – Liquefied Petroleum Gases (LPG) – Power Alcohol and Biodiesel. **Combustion of Fuels:** Introduction – Calorific Value – Higher and Lower Calorific Values – Theoretical calculation of Calorific Value – Ignition Temperature – Spontaneous Ignition Temperature – Explosive Range – Flue Gas Analysis (ORSAT Method).

CHAPTER 6: Fuels

INTRODUCTION

The various types of fuels like liquid, solid and gaseous fuels are available for firing in boilers, furnaces and other combustion equipments. The selection of right type of fuel depends on various factors such as availability, storage, handling, pollution and landed cost of fuel.

The knowledge of the fuel properties helps in selecting the right fuel for the right purpose and efficient use of the fuel.

The following characteristics, determined by laboratory tests, are generally used for assessing the nature and quality of fuels.

CLASSIFICATION OF FUELS

Chemical Fuels: It is of two types.

(i) **Primary Fuels :** It occurs in nature as such. ex. coal, petroleum, natural gas.

(ii) **Secondary Fuels:** It is derived from primary fuels ex.: coke, gasoline, coal gas.

Primary Fuel or Natural Fuel

Primary Fuel or Natural Fuel

Solid	Liquid	Gaseous
Wood	Crude oil	Natural gas
Peat		
Lignite		
Coal		
Dung		

Secondary or Derived Fuel

Secondary or Derived Fuel

Solid	Liquid	Gaseous
Coke	Tar	Coal Gas
Charcoal	Kerosene	Water gas
Petroleum	Diesel	Oil gas
Coke	Petrol	Bio gas
Coal	Fuel oil	Blast furnace gas
Briquette	Synthetic Gasoline gas	Coke over gas

I. SOLID FUELS

COAL

Coal is a highly carbonaceous matter that has been formed as a result of alteration of vegetable matter (eg., plants) under certain favourable conditions. It is chiefly composed of C, H, N and O besides non-combustible inorganic matter.

The successive stages in the transformation of vegetable matter into coal are– wood, peat, lignite, bituminous coal, steam coal and anthracite. Anthracite is probably the purest form of coal and contains 95 % carbon.

CLASSIFICATION OF COAL

(a) Peat

1. Peat is the first stage in the formation of coal.
2. Its calorific value is about 4000-5400 k cal/kg.
3. It is an uneconomical fuel due to its high proportion of (80 -90%) moisture and lower calorific value.
4. It is a brown fibrous mass.

(b) Lignite

1. Lignite is an intermediate stage in the process of coal
2. Formation.
3. Its calorific value is about 6500-7100 kcal/kg
4. Due to the presence of high volatile content, it burns with long smoky flame.

(c) Bituminous Coal

Bituminous coal is further sub-classified on the basis of its carbon content into three types as:

1. Sub- bituminous coal,
2. Bituminous coal and
3. Semi-bituminous coal.

(d) Anthracite

1. Anthracite is the superior grade of coal.
2. Its volatile, moisture and ash contents are very less.
3. Its calorific value is about 8650 kcal/kg

ANALYSIS OF COAL

The quality of a coal is ascertained by the following two types of analysis are made.

Proximate Analysis

- *Proximate Analysis indicates the percentage by weight of the fixed carbon, volatiles, ash, and moisture content in coal.*

- The amounts of fixed carbon and volatile combustible matter directlycontribute to the heating value of coal.
- Fixed carbon acts as a main heat generator during burning. High volatile matter content indicates easy ignition of fuel.
- The ash content is important in the design of the furnace grate, combustion volume, pollution control equipment and ash handling systems of a furnace.

Significance of Various Parameters in Proximate Analysis

(a) Fixed Carbon

Fixed Carbon is the solid fuel left in the furnace after volatile matter is distilled off. It consists mostly of carbon but also contains some hydrogen, oxygen, sulphur and nitrogen not driven off with the gases. Fixed carbon gives a rough estimate of heating value of coal.

(b) Volatile Matter

Volatile Matters are the methane, hydrocarbons, hydrogen and carbon monoxide, and incombustible gases like carbon dioxide and nitrogen found in coal. Thus the volatile matter is an index of the gaseous fuels present. Typical range of volatile matter is 20 to 35%. The loss in weight of the sample is found out and the % of the volatile matter is calculated as:

$$\text{\% of volatile matter in coal} = \frac{\text{loss in weight of the coal}}{\text{weight of air - dried coal}} \times 100$$

Volatile Matter

- Proportionately increases flame length, and helps in easier ignition of coal.
- Sets minimum limit on the furnace height and volume.
- Influences secondary air requirement and distribution aspects.
- Influences secondary oil support

(c) Ash Content

Ash is an impurity that will not burn. Typical range is 5 to 40%. After the analysis of volatile matter, the crusible with residual coal sample is heated without lid as 700 $\pm 50^{o}\,\mathrm{C}$ for 1/2 an hour in a muffle furnace. The loss in weight of the sample is found out and the % of ash content is calculated as:

$$\text{\% of ash content in coal} = \frac{\text{weight of ash formed}}{\text{weight of air - dried coal}} \times 100$$

Ash

- Reduces handling and burning capacity.
- Increases handling costs.
- Affects combustion efficiency and boiler efficiency
- Causes clinkering and slagging.

(d) Moisture Content

Moisture in coal must be transported, handled and stored. Since it replaces combustible matter, it decreases the heat content per kg of coal. Typical range is 0.5 to 10% . The loss in weight of the sample is found out and the % of moisture is calculated as:

$$\text{\% of moisture in coal} = \frac{\text{loss in weight of the coal}}{\text{weight of air - dried coal}} \times 100$$

Moisture

- Increases heat loss, due to evaporation and superheating of vapour
- Helps, to a limit, in binding fines.
- Aids radiation heat transfer.

(e) Sulphur Content

Typical range is 0.5 to 0.8% normally.

Sulphur

- Affects clinkering and slagging tendencies
- Corrodes chimney and other equipment such as air heaters and economizers
- Limits exit flue gas temperature

Ultimate Analysis

The ultimate analysis indicates the various elemental chemical constituents such as Carbon, Hydrogen, Oxygen, Sulphur, etc. It is useful in determining the quantity of air required for combustion and the volume and composition of the combustion gases. This information is required for the calculation of flame temperature and the flue duct design etc.

(a) Determination of carbon and hydrogen in coal

A known amount of coal is burnt in presence of oxygen thereby converting carbon and hydrogen of coal into –

i. $CO_2\,(C + O_2 \longrightarrow CO_2)$ and

ii. $H_2O\,(H_2 + 1/2\,O_2 \longrightarrow H_2O)$

respectively. The products of combustion CO_2 and H_2O are passing over weighed tubes of anhydrous $CaCl_2$ and KOH which absorb H_2O and CO_2 respectively.

The increase in the weight of $CaCl_2$ tube represents the weight of water formed while the increase in the weight of KOH tube represents the weight of CO_2 formed.

The percentage of carbon and hydrogen in coal can be calculated in the following way-

The weight of coal sample taken $= x\ g$

The increase in the weight of KOH tube $= y\ g$

The increase in the weight of $CaCl_2$ tube $= z\ g$

Consider the following reaction:

$$C(12) + O_2 \longrightarrow CO_2\,(44)$$

44 g of CO_2 contains 12 g of carbon

Therefore $y\ g$ of CO_2 contains $= \dfrac{y\ x\ 12}{44\ x}$ g of carbon

$x\ g$ of coal contains $= \dfrac{12\,y}{44}$ g carbon

% of carbon in coal $= \dfrac{12\,y}{44\,x} \times 100$ (or)

% of carbon in coal $= \dfrac{\text{increase in weight of KOH tube}}{\text{weight of coal sample taken}} \times \dfrac{12}{44} \times 100$

Significance

It is the sum total of fixed carbon and the carbon present in the volatile matters like CO, CO_2, hydrocarbons. Thus, total carbon is always more than fixed carbon in any coal. High total carbon containing coal will have higher calorific value.

(b) Determination of hydrogen

Consider the following reaction:

$$H_2(2) + \frac{1}{2}O_2 \longrightarrow H_2O(18)$$

18 g of water contains 2 g of hydrogen.

$z\,g$ of water contains $= \frac{2z}{18}$ of hydrogen

$x\,g$ of coal contains $= \frac{2z}{18}$ g of hydrogen

% of hydrogen in coal $= \frac{2z}{18x} \times 100$ (or)

% of hydrogen $= \frac{\text{increase in weight of } CaCl_2 \text{ tube}}{\text{weight of coal sample taken}} \times \frac{2}{18} \times 100$

Significance

It increases the calorific value of the coal. It is associated with the volatile matter of the coal. When the coal containing more of hydrogen is heated, it combines with nitrogen present in coal forming ammonia. Ammonia is usually recovered as $(NH_4)_2SO_4$, a valuable fertilizer.

(c) Determination of Nitrogen

This is done by Kjeldhal's method: A known amount of powdered coal is heated with concentrated sulphuric acid in the presence of K_2SO_4 and $CuSO_4$ in a long necked Kjeldhal's fask. This converts nitrogen of coal to ammonium sulphate. When the clear solution is obtained (ie., the whole of nitrogen is converted into ammonium sulphate), it is heated with 50 % NaOH solution and the following reaction occurs:

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

The ammonia thus formed is distilled over and is absorbed in a known quantity of standard 0.1 NH_2SO_4 solution. The volume of unused 0.1 NH_2SO_4 is then determined by titrating against standard NaOH solution. Thus, the amount of acid neutralized by liberated ammonia from coal is determined using the formula.

$$\% \text{ of Nitrogen in Coal} = \frac{14 \times \text{volume of acid used} \times \text{normality}}{1000\,x} \times 100$$

$$= \frac{1.4 \times \text{volume of acid used} \times \text{normality}}{x}$$

Significance

Presence of nitrogen decreases the calorific value of the coal. However, when coal is carbonized, its N_2 and H_2 combine and form NH_3. Ammonia is recovered as $(NH_4)_2SO_4$, a valuable fertilizer.

(d) Determination of sulphur in coal

A known amount of coal is burnt completely in Bomb calorimeter in presence of oxygen.

Ash thus obtained contains sulphur of coal as sulphate which is extracted with dil. HC*l*.

The acid extract is then treated with $BaCl_2$ solution to precipitate sulphate as $BaSO_4$. The precipitate is filtered, washed, dried and weighed. From the weight of $BaSO_4$, the percentage of sulphur in coal is calculated in the following way.

The weight of coal sample taken $= x\ g$

The weight of $BaSO_4$ precipitate $= y\ g$

Consider the following equations:

$$S(32) + 2O_2 \longrightarrow SO_4 \xrightarrow{BaCl_2} BaSO_4(233)$$

233 g of $BaSO_4$ contains 32 g of sulphur

Therefore, $y\ g$ of $BaSO_4$ contains $= \frac{32\,y}{233}$ g sulphur

Therefore, $x\ g$ of coal contains $= \frac{32\,y}{233}$ g sulphur

% of sulphur in the coal $= \frac{32\,y}{233} \times 100$

Significance

It increases the calorific value of the coal, yet it has the following undesirable effect.

The oxidation products of sulphur (SO_2, SO_3) especially in presence of moisture forms sulphuric acid which corrodes the equipment and pollutes the atmosphere.

(e) Determination of oxygen in coal

It is calculated indirectly in the following way-

% of oxygen in coal = 100 – % (C + H + N + S + ash).

Significance

The less the oxygen content, the better is the coal. As the oxygen content increases, its moisture holding capacity also increases.

CARBONIZATION

Carbonization (or carbonisation) is the term for the conversion of an organic substance into carbon or a carbon-containing residue through pyrolysis or destructive distillation. It is often used in organic chemistry with reference to the generation of coalgas and coal tar from raw coal.

Manufacture of Metallurgical Coke by Otto Hoffmann's Method

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

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, 3-4m 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 ie. 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.

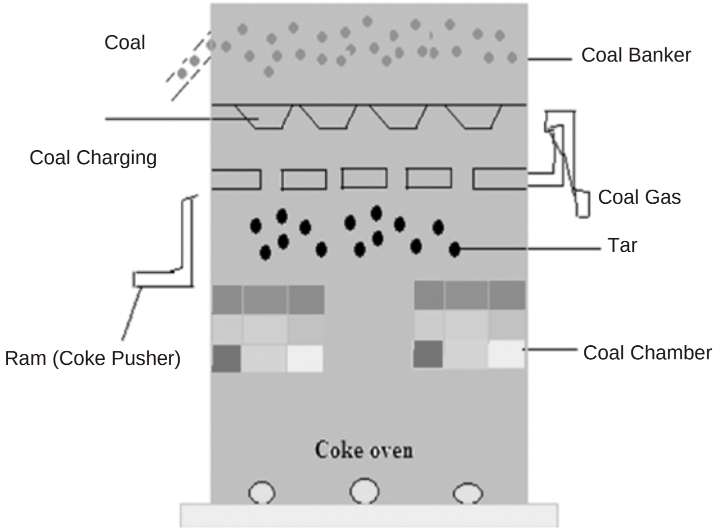


Figure 6.1 : Otto-Hoffmann's Coke Oven

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°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. 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%.

Characteristics of Metallurgical Coke

The most important industrial fuel is the metallurgical coke. This is used in the metallurgical industry, especially in the blast furnace. A good metallurgical coke must have following requirements:

- ***Purity:*** Low moisture and ash content are desirable in metallurgical coke. It must contain minimum percentage of phosphorous and sulphur.
- ***Porosity:*** High porosity is desirable in furnace coke to obtain high rate of combustion.
- ***Strength:*** The coke should be hard and strong to withstand pressure of ore, flux etc. in the furnace.
- ***Size:*** Metallurgical coke must be uniform and medium size.
- ***Calorific value:*** This should be high.
- ***Combustibility:*** It should burn easily.
- ***Reactivity:*** It refers to its ability to react with O_2, CO_2, steam and air. The metallurgical coke must have low reactivity.
- ***Cost:*** It must be cheap and readily available.

II. LIQUID FUELS

PETROLEUM

Petroleum or crude oil is a dark greenish -brown, viscous oil found deep in earth crust. It is composed mainly of various hydrocarbons (like straight-chain paraffins, cycloparaffins or naphthalenes, olefins and aromatics), together with small amounts of organic compounds containing oxygen, nitrogen and sulphur.

The average composition of crude oil is as follows:

Constituents	*Percentage (%)*
C	80-87
H	11-15
S	0.1-3.5
N + O	0.1-0.5

In countries like Germany and South Africa which do not have extensive petroleum deposits, motor fuels are derived from non-petroleum sources. Petroleum can be produced from coal by the following two methods.

6.7.1 Manufacutre of Synthetic Petrol (Bergius Process)

This method was first proposed by Bergius in Germany. It consists of converting low grade coals such as bitminuous coal into liquid and gaseous fuels by hydrogenating them in presence of iron oxide as catalyst.

The raw materials used in the process are coal dust, heavy oil and nickel oleate or tinoleate. A coal paste is prepared by mixing coal dust with heavy oil and catalyst. It is then pumped into the converter where the paste is heated to 450 °C under 200-250 atmosphere in pressure of hydrogen.

The reaction products mainly contain mixture of petroleum hydrocarbons

$$\begin{tikzcd}
\text{Coal dust suspended in heavy oil} + H_2 \arrow[r, "450\,^\circ\text{C}"] & \text{Mixture of hydrocarbons} \arrow[d, "\text{Condensation}"] \\
& \text{Crude Oil}
\end{tikzcd}$$

Since the reaction is exothermic, the vapours leaving the converters are condensed in the condenser to give synthetic petroleum or crude oil. The oil is then fractionally distilled to give:

(i) Petrol , (ii) Middle Oil , (iii) Heavy Oil.

Middle Oil is again hydrogenated in presence of solid catalyst to produce more amount of petroleum Heavy oil is used for making paste with fresh coal dust which is required for this process.

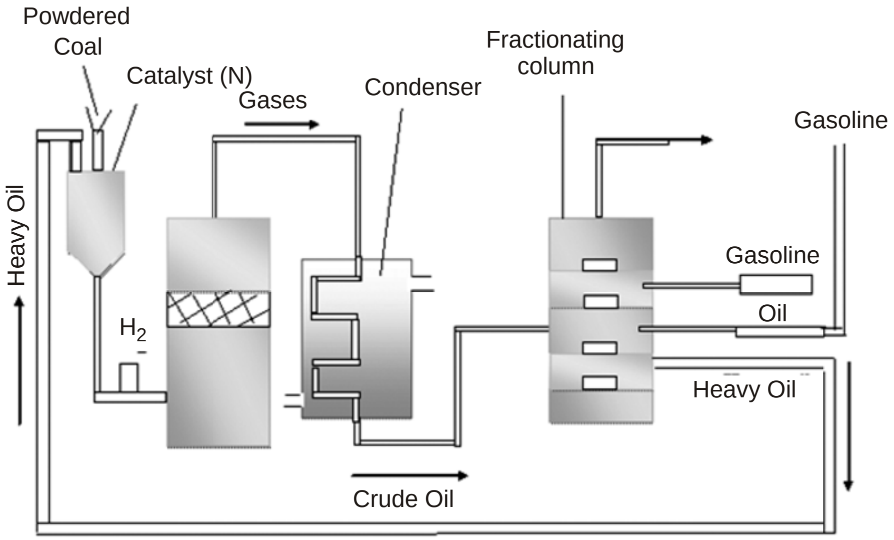


Figure 6.2 : Bergius Process

KNOCKING

In an internal combustion engine, a mixture of gasoline (petroleum) vapour 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 stroke of the piston is known as the compression ratio. The efficiency of an internal combustion engine increases with the compression ratio.

"Knocking is a kind of explosion due to rapid pressure rise occurring in an IC engine".

However, successful high compression ratio 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 fuelair mixture gets ignited instantaneouslyproducing an explosive violence known as knocking. The knocking results in loss of efficiency, since this ultimately decreases the compression ratio. The phenomenon of knocking is not yet fully understood. However, it is noted that the tendency of fuel constituents to knock is in the following order:

Straight chain paraffins (n-paraffins) > branched chain paraffins (iso paraffins) > olefins> cycloparaffins (naphthalenes) > aromatics.

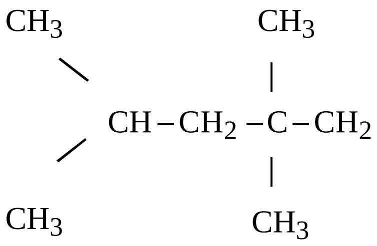
Thus, olefins of the same carbon chain length possess better antiknock properties than the corresponding paraffins and so on.

OCTANE NUMBER

The most common way of expressing the knocking characteristics of a combustion engine fuel is by octane number introduced by Edger in 1972. It has been found that n-heptane, $3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$, knocks very badly and hence, its antiknock value has been arbitrarily given zero. On the other hand, iso-octane (2,2,4 –trimethylpentane) gives very little knocking, so its antiknock 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 iso-octane in a mixture of iso-octane and n-heptane", which matches the fuel under test in knocking characteristics.

Thus, if a sample of petrol gives as much of knocking as a mixture of 75 parts of iso-octane and 25 parts of n-heptane, then its octane number is taken as 75. The octane ratings of some common hydrocarbons are given in the table.



Iso-octane
(octane number = 100)

$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$

n-heptane
(octane number = 0)

S.No	Hydrocarbon	Octane Number
1.	Benzene	100+
2.	Isopentane	90
3.	Cyclohexane	77
4.	2-metyl pentane	71
5.	n-pentane	62

Fuels with octane rating greater than 100 are quite common nowadays and they are rated by comparison with a blend of iso-octane with tetra ethyl lead (TEL) which greatly diminishes the knocking tendency of any hydrocarbon with which it is mixed. The value of octane number in such cases is determined by extrapolation.

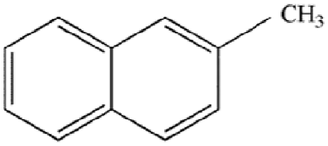
DIESEL OIL

- It is relatively a high boiling point fraction of petroleum obtained between 250 - 320°C.
- It is a mixture of hydrocarbons in terms of carbon atoms C_{15}-C_{18}
- Its calorific value is about 11,000 kcals/kg. It is used as fuel for compression ignition engine.
- Its antiknock value can be improved by doping with isoamyl nitrate.

CETANE NUMBER

In a diesel engine, the fuel is exploded not by a spark but by the application of heat and pressure. Dieselengine fuels consist oflonger 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-methyl naphthalene
Cetane number = 0

$CH_3\text{-}(CH_2)_{14}\text{-}CH_3$
n-hexadecane
Cetane number = 100

Thus, cetane number is defined as “the percentage of hexa decane present in a mixture of hexa decane and α–methyl naphthalene, which has the same ignition lag as the fuel under test”.

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, and 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.

The cetane number decreases in the following order:

straight chain paraffins > cycloparaffins > olefins > branched paraffins > aromatics.

III. GASEOUS FUELS

NATURAL GAS

Methane is the main constituent of Natural gas and accounting for about 95% of the total volume. Other components are: Ethane, Propane, Butane, Pentane, Nitrogen, Carbon Dioxide, and traces of other gases. Very small amounts of sulphur compounds are also present. Since methane is the largest component of natural gas, generally properties of methane are used when comparing the properties of natural gas to other fuels.

Natural Gas is a high calorific value fuel requiring no storage facilities. It mixes with air readily and does not produce smoke or soot. It has no sulphur content. It is lighter than air and disperses into air easily in case of leak. A typical comparison of carbon contents in oil, coal and gas is given in the Table.

Table. Comparison of Chemical composition of various fuels

Content	Fuel oil	Coal	Natural gas
Carbon	84	41.11	74
Hydrogen	12	2.76	25
Sulphur	3	0.41	-
Oxygen	1	9.89	Trace
Nitrogen	Trace	1.22	0.75
ash	Trace	38.63	-
water	Trace	5.98	-

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 × 104 L or 20 m^3 of natural gas at 1 atmospheric pressure. It is derived from natural gas and the main constituent of CNG is methane.

The average composition of CNG is as follows:

Constituents	Percentage %
Methane	88.5
Ethane	5.5
Propane	3.7
Butane	1.8
Pentane	0.5

Properties

(i) CNG is comparatively much less pollution causing fuel as it produces less CO, ozone and hydrocarbons during combustion.

(ii) During it s combustion, no sulphur and nitrogen gases are evolved.

(iii) No carbon particles are ejected during combustion.

(iv) It is less expensive than petrol and diesel.

(v) The ignition temperature of CNG is 550

(vi) CNG is a better fuel than petrol/diesel for automobiles.

(vii) 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/m^3.

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.

The average composition of LPG is as follows:

Constituents	**Percentage %**
n-Butane	38.5
Iso Butane	37.0
Propane	24.5

Power Alcohol

When ethyl alcohol is used as fuel in internal combustion engine, it is called as "power alcohol". Generally ehty alcohol is used as its 5-25% mixture with petrol.

Advantages of Power Alcohol:

- Ethyl alcohol has good antiknocking property and its octane number is 90, while the octane number of petrol is about is 65. Therefore, addition of ethyl alcohol increases the octane number of petrol.

- Alcohol has property of absobing any traces of water if present in petrol.
- If specially designed engine with higher compression ratio is used, then disadvantage of lower Calorific value of ethyl alcohol can be overcome.
- Ethyl alcohol contains ‘O’ atoms, which helps for complete combustion of power alcohol and the polluting emissions of CO, hydrocarbon,particulates are reduced largely.
- Use of ethyl alcohol in petrol reduces our dependence on foreign countries for petrol and saves foreign considerably.
- Power alcohol is cheaper than petrol.

Disadvantages of Power Alcohol:

- Ethyl alcohol has calorific value 7000cal/gm much lower than calorific value of petrol 11500cal/gm. Use of power alcohol reduces power output upto 35%.
- Ethyl alcohol has high surface tension and its atomisation, especially at lower temperature, is difficult causing starting trouble.
- Ethyl alcohol may undergo oxidation reaction to form acetic acid, which corrodes engine parts.
- As ethyl alcoholcontains ‘O’ atoms, the amount of air require for complete combustion of power alochol is lesser and therefore carburettor and engine need to be modified, when only ethyl alcohol is used as fuel.

Biodiesel

A fuel derived from organic oils, such as vegetable oil, rather than petroleum. Biodiesel’s use and production are increasing. It’s typically used for aircraft, vehicles and as heating oil.

Vegetable oils comprise of 90–95% triglycerides with small amount of diglycerides, free fatty acids, phospholipids, etc. The viscosity of vegetable oils are higher and their molecular weights are in the range of 600 to 900, which are about 3 times higher than those of the diesel fuels.

Problems in using Vegetable Oils directly

(i) As the viscosity of vegetable oils are high, atomization is very poor and hence inefficient mixing of oil with air leads to incomplete combustion.

(ii) Oxidation and Thermal polymerization of vegetable oils cause deposit formation.

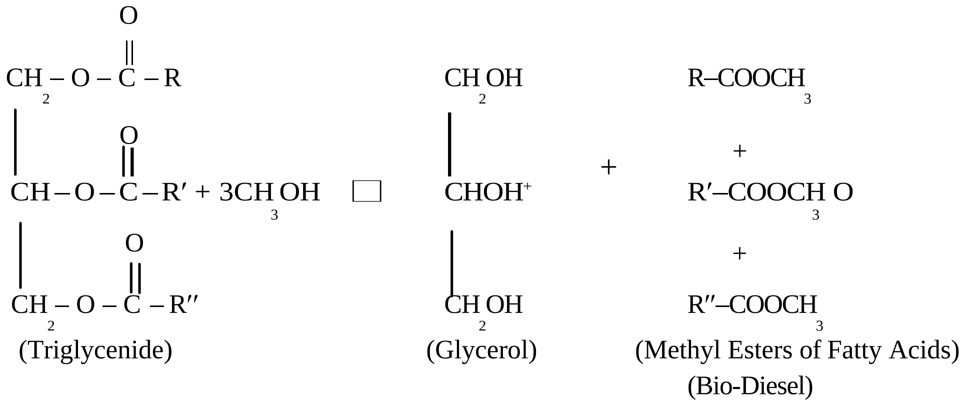
(iii) Their high velocity and consequent high flash point lead to more deposite formation.

Manufacture: Trans-Esterification (or) Alcoholysis

The above problems are overcome by reducing the viscosity of the vegetable oils by the process known as **trans-esterification or alcoholysis**. Alcoholysis is nothing but displacement of alcohol from an ester by another alcohol.

It involves treatment of vegetable oil (sunflower oil, palm oil, soyabean oil, mustard oil, etc.) with excess of methanol in the presence of catalyst to give mono ethy esters of long chain fatty acid and glycerine. It is allowed to stand for some time and glycerine is separated. □

Alcoholysis reaction is represented as: $-0.09\text{H} \times 587\ kcal/kg$



$$\begin{array}{lclcl}
\overset{\overset{\text{O}}{\|}}{\text{CH}_2-\text{O}-\text{C}-\text{R}} & & \text{CH}_2\text{OH} & & \text{R–COOCH}_3 \\
| & & | & & + \\
\text{CH}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{R}' + 3\text{CH}_3\text{OH} & \square & \text{CHOH}^{+} & + & \text{R}'\text{–COOCH}_3\text{ O} \\
| & & | & & + \\
\text{CH}_2-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{R}'' & & \text{CH}_2\text{OH} & & \text{R}''\text{–COOCH}_3 \\
\text{(Triglycenide)} & & \text{(Glycerol)} & & \text{(Methyl Esters of Fatty Acids)} \\
 & & & & \text{(Bio-Diesel)}
\end{array}$$

Methyl esters of fatty acids, thus formed, are called “Bio-diesel”. **Bio diesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or fats**.

Advantages

1. It can be produced from renewable, domestic resources.
2. Biodiesel is energy efficient (The total fossil fuel energy efficiency of biodiesel is 320% vs. 83% for petroleum diesel) (National Biodiesel Board, 1998)
3. It can be used directly in most diesel engine applications.
4. It can reduce global warming and tailpipe emissions (–41%)
5. It is nontoxic and biodegradable.
6. It is a good solvent and mayclean out fuel line and tank sediments. (Note that this may result in fuel filter clogging during initialuse)

Limitations

1. It contains approximately 8% less energy per gallon.
2. It generally has a higher cloud and pour point (will freeze at a higher temp) than conventional diesel.
3. It is not compatible with some hose and gasket materials, which may cause them to soften, degrade, and rupture.
4. It is not compatible with some metals and plastics.
5. It may increase nitrogen oxide emissions

CHAPTER 7: Combustion of Fuels

COMBUSTION OF FUELS

Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and industrial purposes. Eg., Wood, Charcoal, Coal, Kerosene, Petrol, Producer gas, Oil gas, LPG etc., During the process of combustion of a fuel (like coal), the atoms of carbon, hydrogen, etc. combine with oxygen with the simultaneous liberation of heat at a rapid rate.

$$\text{Fuel} + \text{Oxygen} \longrightarrow \text{Products} + \text{Heat}$$

Calorific Value

Calorific Value of a Fuel is *"the total quantity of heat liberated, when a unit mass (or volume) of the fuel is burnt completely"*.

Units of Heat:

(1) Calorie □ is the amount of heat required to raise the temperature of one gram of water through one degree centigrade (15-16 °C).

(2) Kilocalorie □ is equal to 1,000 calories. This is the unit of metric system and may be defined as "the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade. Thus, 1 kcal = 1,000 calories.

(3) British Thermal Unit (BTU) □ is defined as "the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit (60-61°F). This is the English system unit.1 BTU = 252 cal = 0.252 kcal and 1 kcal = 3.968 BTU

(4) Centigrade Heat Unit (CHU) □ *i*s "the quantity of heat required to raise the temperature of 1 pound of water through one degree centigrade".

Thus, 1 kcal = 3.968 BTU = 2.2 CHU.

Higher or Gross Calorific Value (GCV)

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 (NCV)

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.

∴ NCV = GCV – Latent heat of condensation of water vapour produced

= GCV – Mass of hydrogen × 9 × Latent heat of condensation of water vapour

Theoretical Calculation of Calorific Value

The calorific value of fuel can be *approximately* computed by noting the amounts of the constituents of the fuel. The higher calorific value of some of the chieg combustible constitutents of fuel are tabulated below:

Table : Calorific values of fuel constituents

Constituent	*Hydrogen*	*Carbon*	*Sulphur*
HCV (kcal/kg)	34,500	8,080	2,240

The oxygen, if present in the fuel, is assumed to be present in combined form with hydrogen, i.e., in the form of ***fixed hydrogen*** (H_2O). so, the amount of hydrogen available for combustion

= Total mass of hydrogen in fuel – Fixed hydrogen

= Total mass of hydrogen in fuel $-\left(\frac{1}{8}\right)$ Mass of oxygen in the fuel

(ie., 8 parts of oxygen combine with one part of hydrogen to form H_2O)

Dulong's Formula for calorific value from the chemical composition of fuel is:

$$\text{HCV} = \frac{1}{100}\left[8,080\text{ C} + 34,500\left(\text{H} - \frac{\text{O}}{8}\right) + 2240\right]\text{kcal / kg}$$

where C,H,O and S are the percentages of carbon, hydrogen, oxygen and su;phur in the fuel respectively. In this formula, oxygen is ssumed to be present in combinatio with hydrogen as water, and

$$\text{LCV} = \left[\text{HCV} - \frac{9}{100}\text{H} \times 587\right]\text{kcal / kg} = [\text{HCV} - 0.09\text{H} \times 587]\text{ kcal / kg}$$

This is based on the fact that 1 part of H by mass gives 9 parts of H_2O, and latent heat of stam is 587 kcal/kg.

PROBLEMS BASED ON CALORIFIC VALUE

Problem 1: Calculate the gross and net calorific values of coal having the following compositions, carbon = 85%, hydrogen = 8%, sulphur = 1%, nitrogen = 2%, ash = 4%, latent heat of steam = 587 cal/gm.

Solution:

(i) Gross Calorific Value (GCV)

$$= \frac{1}{100}\left[8080 \times \%\,c + 34500\left(\%\,\text{H} - \frac{\%0}{8}\right) + 2240 \times \%\,s\right]\text{kcal / kg}$$

$$= \frac{1}{100}\left[8080 \times 85 \times 34500\left(8 - \frac{0}{8}\right) + 2240 \times 1\right]\text{kcal / kg}$$

$$= \frac{1}{100}[6,\,86{,}800 + 2,\,76,\,000 + 2240]\text{kcal / kg}$$

$$= \frac{1}{100}\left[9,\ 65,\ 040\right] \text{kcal / kg}$$

$$= 9650.4 \text{ kcal/kg.}$$

(ii) Net Calorific Value (NCV)

$$= \text{GCV} - \frac{9}{100} \text{H} \times 587 \text{ kcal / kg}$$

$$= 9650.4 - \frac{9}{100} \times 8 \times 587 \text{ kcal / kg}$$

$$= 9650.4 - 422.64$$

$$= 9227.76 \text{ kcal / kg.}$$

Problem 2: Calculate the net and gross calorific value of a coal sample having following composition. C = 82%, H = 8%, 0 = 5%, N = 1.4% and ash = 3.6%.

Solution:

(i) GCV

$$= \frac{1}{100}\left[8080 \times \%\, c + 34500\left(\%\, \text{H} - \frac{\%0}{8}\right) + 2240 \times \%s\right] \text{kcal / kg}$$

$$= \frac{1}{100}\left[8080 \times 82 \times 34500\left(8 - \frac{5}{8}\right) + 0\right] \text{kcal / kg}$$

$$= \frac{1}{100}\left[662560 + 254437.3\right]$$

$$= 9169.8 \text{ kcal / kg .}$$

(ii) NCV

$$= \text{GCV} - \frac{9}{100} \text{H} \times 587 \text{ kcal / kg}$$

$$= 9169.98 - \frac{9}{100} \times 8 \times 587$$

$$= 8747.34 \text{ kcal/kg.}$$

Problem 3: Calculate the gross and net calorific valve of a fuel having following composition 82%, C, 8% H, 5% O, 2.5% S, 1.4% N and 2.1% ash.

Solution: We know that,

$$\text{GCV} = \frac{1}{100}\left[8080\,c + 34500\,(\text{H} - 0/8) + 22405\right]\text{kcal / kg}$$

$$= \frac{1}{100}\left[8080 \times 82 \times 34500\,(8 - 5/8) + 2240 \times 2.5\right]$$

$$= 9225.97 \text{ kcal/kg}$$

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

$$\text{NCV} = 9225.97 - 0.09 \times 8 \times 587$$

$$= 8803.3 \text{ kcal/kg.}$$

IGNITION TEMPERATURE (IT)

It is defined as ***"the lowest temperature to which the fuel must be heated, so that it starts burning smoothly".***

The ignition temperature of coal is about 300°C. In the case of liquid fuels, the ignition temperature is called the flash point, which ranges from 200–400°C. For gaseous fuels, the ignition temperature is in the order of 800°C.

Spontaneous Ignition Temperature (SIT)

When a gaseous mixture of fuel and oxidant is maintained at ambient temperature, reaction rates are extremely slow. Increasing the mixture of temperature, the reaction rate suddenly increases, giving rise to rapid combustion reactions. This condition is referred to as spontaneous ignition and the minimum temperature at which rapid combustion reactions are initiated is called **the *spontaneous ignition temperature*** $[T_{sit}]$.

The factors influencing the spontaneous ignition temperature of given mixture are the balance between heat release and heat loss, as well as the supply of reactants.

For liquid fuels, this parameter is determined using standardized tests, where liquid fuel is dropped into an open air container heated to a known temperature.

The spontaneous ignition temperature is defined as the lowest temperature at which visible or audible evidence of combustion is observed.

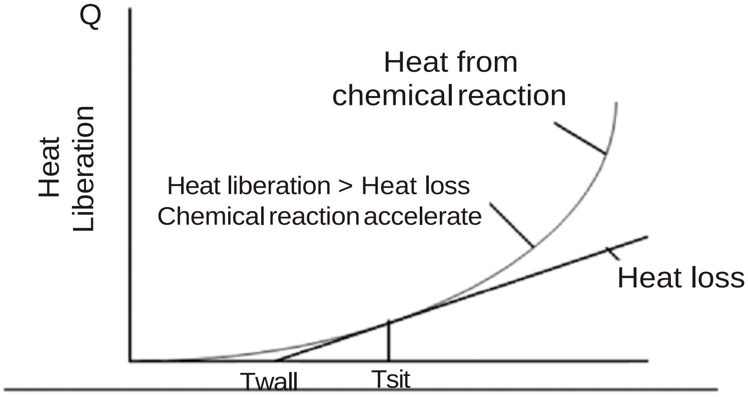


Figure 7.1 : Spontaneous Ignition Temperature

Explosive Range (or) Limits of Inflammability

Most of the gaseous fuels have two percentage limits called upper limit and lower limit. Those limits represent percentage by volume of fuel present in fuel-air mixture. The range covered by these limits is termed as explosive range of the fuel.

For continuous burning the amount of fuel present in the fuel-air mixture should not go below the lower limit or above the upper limit.

For example, the explosive range of petrol is 2-4.5. This means that when the concentration of petrol vapour in petrol-air mixture is between 2 and 4.5 by volume, the mixture will burn on ignition. When the concentration of petrol vapour in petrol-air mixture is below 2% (lower limit) or above 4.5% (upper limit) by volume, the mixture will not burn on ignition.

FLUE GAS ANALYSIS (ORSAT METHOD)

The mixture of gases like SO_2, CO_2, O_2, CO etc. coming out from the combustion chamber is called flue gas.

Analysis:

The flue gas analysis is carried out by using Orsat's apparatus. The analysis of flue gas generally deals with the determination of CO_2, O_2 and CO by absorbing them in the respective solution of KOH, alkaline pyrogallol and ammonium cuprous chloride.

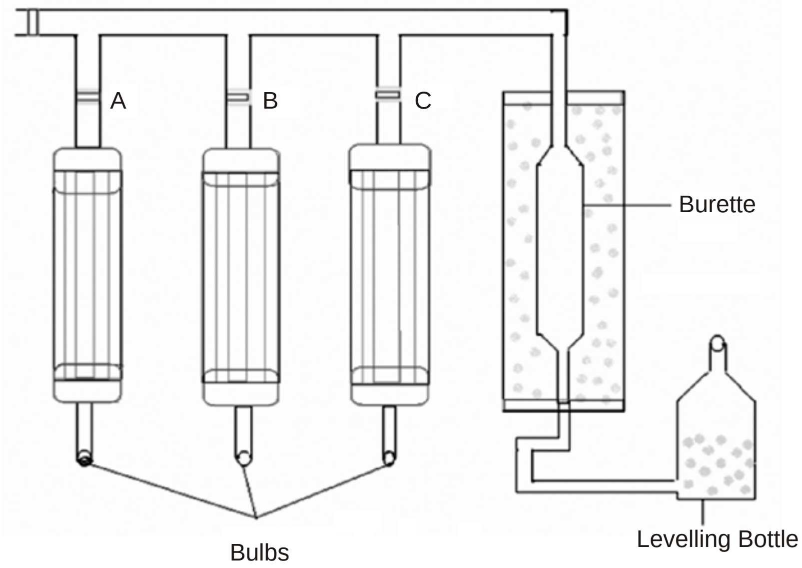


Figure 7.2 : Orsat's Apparatus

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 CO_2, O_2 and CO respectively. The lower end of the burette is connected to the leveling bottle by means of rubber tube.

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.

Importance of Flue Gas Analysis:

(i) The analysis gives the idea of whether a combustion process is complete or not.

(ii) The C and H present in a fuel undergo combustion forming CO_2 and H_2O respectively. Any N present is not at all involved in the combustion. ie., the products of combustion are CO_2, H_2O and N_2.

(iii) If analysis of a flue gas indicates the presence of CO; it is suggestive of incomplete combustion (Wastage of heat is inferred)

(iv) If there is considerable amount of oxygen, it shows that there is excess supply of O_2 although combustion would have been complete.

(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 +200g 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.

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