UNIT V
FUELS AND COMBUSTION

1. FUELS

Fuel is a combustible substance which on burning produces large amount of heat. This heat can be used economically for domestic and industrial purposes.

\[
\text{Fuel} + \text{air}(O_2) \rightarrow \text{Products} + \text{heat}
\]

The total quantity of heat given out by a unit mass of fuel on combustion depends mainly on two elements, namely carbon and hydrogen.

\[
\begin{align*}
C + O_2 & \rightarrow \text{CO}_2 + 94 \text{ kcals} \\
2H_2 + O_2 & \rightarrow \text{H}_2\text{O} + 68.5 \text{ kcals}
\end{align*}
\]

1.1 Classification of Fuels

The classification of fuels may be divided into two types based on their occurrence and physical state

(i) Primary fuels which occur in nature

(ii) Secondary fuel which is derived from the primary fuel

Fuels may also be classified into three groups:


<table>
<thead>
<tr>
<th>Sources</th>
<th>Solid</th>
<th>Liquid</th>
<th>Gaseous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary (Natural)</td>
<td>Wood, Coal, Anthracite</td>
<td>Crude oil or petroleum</td>
<td>Natural gas</td>
</tr>
<tr>
<td>Secondary (Synthetic)</td>
<td>Coke, Charcoal, Nitro cellulose</td>
<td>Gasoline, Diesel oil, Kerosene and Coal tar</td>
<td>Coal gas, Water gas and Producer gas</td>
</tr>
</tbody>
</table>

1.2 Characteristics of a Good Fuel

i) High calorific value

ii) Moderate ignition temperature.

iii) Moderate velocity of combustion.
iv) Low moisture content.

v) Low contents of non-combustible material.

vi) Products of combustion should not be harmful.

1.3 Coal

Coal is the most important solid fuel that is derived from vegetable matter. It is chiefly composed of carbon, hydrogen, nitrogen, oxygen and sulphur, besides non-combustible inorganic matter.

1.3.1 Analysis of Coal

Coal composition depends on its source and age. The coal is composed of mixture of organic compounds along with some inorganic matter. The calorific value of coal depends upon its composition.

To confirm the quality or rank of the coal, two types of analysis are carried out:

i) Proximate analysis

ii) Ultimate analysis

i) Proximate analysis

This method is used for determination of percentage of moisture content, volatile matter, ash and fixed carbon in the coal. The proximate analysis gives information about the practical utility of coal.

a) Determination of Moisture: A known amount of the finely powdered coal sample is taken in a silica crucible. Then crucible is placed in an electric hot air-oven, maintained at temperature of 105-110° C. The crucible is allowed to remain in oven for 1 hour.

After one hour, crucible is taken out with the help of tongs, cooled in a desiccator and weighed. The process of heating, cooling and weighing is repeated a number of times till the weight of the crucible containing coal becomes constant. Loss of weight of coal is due to moisture content.

\[
\text{Percentage of Moisture} = \frac{\text{Loss in weight}}{\text{Weight of Coal taken}} \times 100
\]

b) Determination of volatile matter:

The dried sample of coal left in the crucible in first experiment is then covered with a lid
and placed in an electric furnace, maintained at a temperature of 950° C. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then cooled in a desiccator and weighed. The process of heating, cooling and weighing is repeated a number of times till the weight of the crucible containing coal (now volatile matter removed) becomes constant. Loss of weight of coal is due to volatile matter.

\[
\text{Percentage of Volatile matter} = \frac{\text{Weight of volatile matter removed}}{\text{Weight of moisture free Coal}} \times 100
\]
c) **Determination of ash:**

The residual coal in the crucible in the above experiment is then heated without lid in a muffle furnace at 700° - 750°C for 30 minutes. After 30 minutes crucible is cooled in a desiccator and weighed.

The process of heating, cooling, and weighing is repeated a number of times till the weight of the crucible become constant. Residue obtained is known as ash.

\[
\text{Percentage of Ash} = \frac{\text{Weight of ash formed}}{\text{Weight of dry Coal sample}} \times 100
\]

**d) Determination of fixed carbon:**

It is determined indirectly by deducting the moisture content, ash and volatile matter from 100.

Percentage of fixed carbon = 100 – (% of moisture + % of volatile matter + % of ash)

**Significance of proximate analysis or Importance of proximate analysis**

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

<table>
<thead>
<tr>
<th>Coal composition</th>
<th>Merits</th>
<th>Demerits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>Presence of small quantity of moisture in coal makes the coal bed uniform and also it reduces the amount of fly ash.</td>
<td>Calorific value gets reduced. Moisture increases the transport charges.</td>
</tr>
<tr>
<td><strong>Volatile matter:</strong></td>
<td>Less volatile matter containing coal is suitable for coal gas manufacture and metallurgical coke.</td>
<td>Burns with smoky flame causes air pollution. It lowers the calorific value of coal. Its disposal is a big problem. Ash causes hindrance in the flow of heat.</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>CO, H₂, CH₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂, N₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ash:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica, alumina, magnesia, lime etc.</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Fixed carbon</strong></td>
<td>If fixed carbon percentage is higher in coal then calorific value, calorific intensity will be high.</td>
<td></td>
</tr>
</tbody>
</table>
1.4 Coke Manufacture- Carbonisation of Coal

When coal is heated strongly in the absence of air, it loses volatile matter and converted into white, lustrous, dense, strong porous and coherent mass known as coke. This process of converting coal into coke is called carbonisation.

1.4.1 Types of Carbonisation

Depending in the temperature of carbonisation the following three types of carbonisation are usually performed.

i) Low temperature carbonisation (500 to 700°C)
ii) Medium temperature carbonization (700 to 900°C)
iii) High temperature carbonization (above 900°C)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Low temperature carbonisation</th>
<th>High temperature carbonisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Heating temperature</td>
<td>500-700°C</td>
<td>1000-1200°C</td>
</tr>
<tr>
<td>2. Yield</td>
<td>75%</td>
<td>70%</td>
</tr>
<tr>
<td>3. VM content</td>
<td>5-15%</td>
<td>1-3%</td>
</tr>
<tr>
<td>4. Calorific value</td>
<td>6500-9500 cal g⁻¹</td>
<td>5500-6000 cal g⁻¹</td>
</tr>
<tr>
<td>5. Mechanical strength</td>
<td>Not mechanically strong</td>
<td>Good</td>
</tr>
<tr>
<td>6. Use</td>
<td>For domestic purposes</td>
<td>For metallurgical purposes</td>
</tr>
</tbody>
</table>

1.4.3 Coking and Non coking(caking) Coals

All types of coal cannot be converted into coke. Coals on heating first loose moisture and volatile matter and at high temperatures the mass becomes soft plastic and fuses to give coherent mass. Such coals are called caking coals.

Coals which form a weakly coherent mass on heating are called non-coking (caking) coals. The coke obtained is hard, porous, strong and dense. Thus all coking coals are caking coals but all caking coals are not coking coals. Only bituminous coal can be coked and it is called coking coals. Anthracite, sub-bituminous and lignite are non-coking coals.
Metallurgical coke can be manufactured by Otto-Hoffmann’s by-product oven method.

1.4.3 Otto-Hoffmann By-Product Oven Method

In this method,

(i) thermal efficiency of carbonisation process is considerably increased by the regenerative system of heat economy

(ii) the valuable by-products like coal gas, ammonia, benzol oil, tar etc., are recovered.

This oven consists (Fig.4.1) of a number of silica chambers, each about 10-12 m long, 3-4 m tall and 0.4 to 0.45 m wide, erected side by side with vertical flues between them. Each chamber has a hole at the top to introduce the coal, a gas off-take and door at each for discharging the coke.

The chambers are packed with finely divided coal and tightly closed. The coke oven is heated to 1200° C by burning gaseous fuel like producer gas. The fuel gases produced during burning pass through two sets of choker-bricks until heated up to 1000° C. The flow of heated flue gases can be reversed to above system of recycling of flue gases to produce heat energy is known as regenerative system of heat economy. Carbonisation takes about 11 to 18 hours.

<table>
<thead>
<tr>
<th>Ammonia Spray</th>
<th>Water Spray</th>
<th>Cold Water Spray</th>
<th>Naphtha</th>
<th>Petroleum Spray</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tar</td>
<td>NH₃</td>
<td>Thalehe Benzene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Silica chambers
When carbonization is completed a ram (coke pusher) pushed the coke produced into a truck. It is quenched by a water spray (wet quenching) or by inert gases (dry quenching).

**Recovery of by-products**

The gas coming out from the oven is known as coke oven gas and is composed of NH₃, H₂S, naphthalene, benzene, tar, etc.,

(i) **Recovery of tar**

The coke oven gas is passed through a tower in which liquor NH₃ is sprayed. Dust and tar along with NH₃ are collected in a tank which is heated by steam coils to recover back the NH₃ sprayed, and used again.

(ii) **Recovery of NH₃**

The coke oven gas free from tar is passed through another tower in which water is sprayed. Here NH₃ goes into solution as, NH₄OH.

(iii) **Recovery of naphthalene**

The gas is then passed through a tower in which water at very low temperature is sprayed. In this tower naphthalene is condensed.

(iv) **Recovery of H₂S**

The gas is then passed through a purifier containing moist Fe₂O₃

\[
\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{S} \rightarrow \text{Fe}_2\text{S}_3 + 3\text{H}_2\text{O}
\]

When all Fe₂O₃ is converted into Fe₂S₃, the purifier is exposed to atmosphere, when Fe₂O₃ is regenerated.

\[
\text{Fe}_2\text{S}_3 + 4\text{O}_2 \rightarrow 2\text{FeO} + 3\text{SO}_2
\]
4FeO + O₂ → 2Fe₂O₃

1.4.4 Characteristics of Metallurgical Coke

The characteristics of metallurgical coke are

i) **Purity**: Metallurgical coke must contain minimum percentage of moisture, ash, sulphur and phosphorous.

ii) **Porosity**: Metallurgical coke must be porous so that oxygen can easily come in contact with carbon of the coke, which ensures the efficient combustion.

iii) **Strength**: Metallurgical coke has to withstand pressure of ore, flux, etc in the furnace so it must have a good mechanical strength.

iv) **Size**: Metallurgical coke must be uniform and medium sized.

v) **Calorific value**: The calorific value should be high

vi) **Cost**: It must be cheap and readily available.

vii) **Combustibility**: Metallurgical coke should burn easily.

**Reactivity**: The reactivity of coke refers to its ability to react with O₂, CO₂, steam and air. Metallurgical coke must have low reactivity.

1.5 Synthetic Petrol

Petrol can be artificially produced by the following methods.

i) Polymerisation

ii) Fischer-Tropsch process

iii) Bergius process
1.5.1 Bergius Process

(Hydrogenation of Coal)

The finely powdered low ash coal is made into a paste with heavy oil or coal tar and then a catalyst composed of tin or nickel oleate is incorporated (Fig. 4.2).

![Diagram of Bergius process]

The coal paste is heated with \( \text{H}_2 \) at 450°C under 200-250°C atmospheric pressure for about 1 to 5 hours. Hydrogenation takes place to form higher saturated hydrocarbons undergoing cracking to yield low boiling liquid hydrocarbons.

\[
\text{Coal Dust} \quad + \quad \text{H}_2 \quad \xrightarrow{\text{catalyst}} \quad 450^\circ \text{C} \quad \xrightarrow{} \quad \text{Mixture of hydrocarbons}
\]
The vapours leaving the converter upon condensation give crude oil or synthetic petroleum. This synthetic petroleum of fractional distillation gives

(i) petrol (ii) middle oil and (iii) heavy oil

The middle oil on hydrogenation in the vapour phase in presence of a solid catalyst gives gasoline.

Heavy oil is again used for making a paste with coal dust. The yield of gasoline is 60% of the coal dust used.

**Fischer – Tropsch Process**

i) In this process coal is first converted to coke and the volatile liquids and tars are removed. Then the coke is heated and steam is passed over it when water gas is produced.

\[
C + H_2O \rightarrow CO + H_2
\]

Coke    Steam    water gas

![Diagram](image)
ii) Synthesis gas is then prepared by mixing water gas and hydrogen in a ratio 2:1. The prepared synthesis gas is passed through ferric oxide for removal of H$_2$S and through a mixture of ferric oxide and sodium carbonate for removal of organic sulphur compounds.

iii) The purified synthesis gas is compressed to 5 to 25 atmospheres over a cobalt-thorium oxide catalyst on Kieselgur at 180 – 200° C. Straight chain paraffins and olefins are obtained as reaction products.

\[
n\ CO + 2n\ H_2 \rightarrow \ C_nH_{2n} + n\ H_2O
\]

\[
n\ CO + (2n+1)\ H_2 \rightarrow \ C_nH_{2n+2} + n\ H_2O
\]

iv) The reaction is exothermic, so out coming hot gaseous mixture is passed through water-cooled condensers, where a liquid resembling crude oil is obtained.

The crude oil thus obtained is sent through fractionating column yield

i) gasoline

ii) High – boiling heavy oil.

The heavy oil is uses fro cracking to get more gasoline.

1.6 Knocking

Knocking is a kind of explosion (sharp metallic sound) produce in the internal combustion engine due to the immature ignition of the air gasoline mixture.

In an internal combustion engine, the gasoline air mixture is highly compressed before it is ignited in order to have maximum efficiency.

Ignition of gasoline air mixture by a spark causes a compression wave to pass through the unburnt gas mixture. Under certain conditions this wave can compress the mixture to above its self-ignition temperature resulting in explosive burning and metallic sound is produced. This is called **knocking**.

**Chemical structure and knocking**

The knocking tendency of a gasoline depends upon the nature and molecular structure of
the hydrocarbons present in the gasoline. The knocking property is in the following order:

Straight chain alkanes > Branched chain alkanes > Alkenes > Naphthenes > Aromatics

1.6.1 Octane Number

The knocking quality of an automobile fuel is measured in terms of octane number.

n-heptane knocks very badly and its anti-knock value has arbitrarily been fixed as zero. Isooctane (2,2,4-trimethylpentane) gives very little knocking and its anti-knock value has been given as 100.

\[
\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 \\
\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3\text{-CH}_3
\]

\[\text{n-heptane}\]

\[
\text{CH}_3\text{-CH}_3\text{-CH}_3\text{-CH}_3\text{-CH}_3\text{-CH}_3
\]

\[\text{Isooctane (2,2,4-trimethyl pentane)}\]

Octane number of a gasoline is the percentage of isooctane in a mixture of isooctane and n-heptane, which matches the fuel under in knocking.

Example: 80-Octane. This fuel has same combustion characteristics as an 80:20 mixture of isooctane and n-heptane.

1.6.1.1 Improvement of anti knocking characteristics of a fuel

Leaded petrol (sweetening of petrol)

The octane number of a fuel can be raised by the addition of a small amount of Tetra Ethyl Lead (TEL) or TEL and diethyl telluride. This process is known as doping. In motor fuel about 0.5 ml of TEL is added per litre of petrol. This petrol is called leaded petrol.

In addition to TEL, a small amount of ethyl fluoride (a mixture of ethylene bromide, ethylene chloride and red dye) is also added.
1.6.2 Cetane Number

In diesel engine, the fuel is exploded not by a spark, but by the application of heat and pressure.

The main characteristic of a diesel engine fuel is that it should easily ignite below compression temperature. The induction lag should be as short as possible. Otherwise the entire amount of oil may get accumulate and will burn suddenly. This cause a great rise in pressure and makes minor explosion in diesel engine.

The cetane number decreases in the following order.

Straight chain alkanes > Cycloalkanes > Alkenes > Branched alkanes > Aromatics

The number used for rating diesel oil is called cetane number.

This represents the spontaneous ignition temperature of the fuel.

\[
\text{CH}_3
\]

\[
\text{CH}_3 \quad \text{CH}_2 \quad \text{CH}_3
\]

2-methyl naphthalene (cetane number = 0)

\[
\text{CH}_3 \quad \text{CH}_2\text{CH}_3
\]

n-hexadecane (cetane number = 100)

Cetane (n-hexadecane) ignites more rapidly than any fuel and its cetane number has been designed as 100. \(\alpha\)-methyl naphthalene ignites slowly than any other fuel and its cetane number is 0.

Cetane number of a fuel is defined as the percentage of cetane present in a mixture of cetane and \(\alpha\)-methyl naphthalene, which matches the fuel under test in ignition.

1.6.2.1 Improvement of Cetane Number

The cetane number of a fuel can be increased by the addition of a small amount of (pre-ignition dopes) ethyl nitrate, isoamyl nitrate and acetone.

1.6.2.2 Diesel Index

According to the American Petroleum Institute (API) the quality of diesel can be expressed by Diesel Index.
The higher the diesel index the better is the quality of the fuel.

\[
\text{Diesel Index} = \frac{\text{Specific gravity (API)} \times \text{Aniline point (F)}}{100}
\]
Relation between Diesel index and cetane number

Diesel Index = Cetane number + 3

1.7 Producer Gas

Composition:

<table>
<thead>
<tr>
<th>Combustible gases</th>
<th>Non-combustible gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co = 22-30%</td>
<td>N₂ = 52-55%</td>
</tr>
<tr>
<td>H₂ = 8-12%</td>
<td>CO₂ = 3%</td>
</tr>
</tbody>
</table>

Producer gas is a mixture of CO and N with small proportion of hydrogen, methane and carbon-di-oxide.

Manufacture:

It is prepared by passing a mixture of air and steam over a bed of red-hot coke (or) coal. Since a low-grade coal can be used in producing producer gas, its cost comes out to below.

![Fig.4.4 Manufacture of Producer gas](image)

Actually, it is considered as the cheapest gaseous fuel. But due to the presence of a large proportion of nitrogen, its calorific value is the lowest of all gaseous fuels.

When a mixture of air and steam is passed over red hot coke or coal bed at about 1000° to 1100°C producer gas is formed. The following reactions take place in different zones of the fuel bed.

Reactions: The gas production reactions can be divided into two zones as follows.
i) **Combustion (or) Oxidation zone**

The solid fuel is fed at the top of this refractory lined reaction vessel and air mixed with a very little steam is injected from bottom. In lower part of furnace carbon from coal combines with oxygen of air to form carbon monoxide and carbon-di-oxide. The temperature of this zone is about 1,100°C

\[ C + O_2 \rightarrow CO_2 \text{ (Oxidation)} \]

ii) **Reduction zone**

This is the middle part of the fuel bed. Here CO\(_2\) and steam are reduced. Here, CO\(_2\) and steam move up through red hot fuel bed and the following reactions take place.

\[
\begin{align*}
C + CO_2 & \rightarrow 2CO \text{ (Reduction)} \\
C + H_2O & \rightarrow CO + H_2 \\
C + 2H_2O & \rightarrow CO_2 + 2H_2
\end{align*}
\]

Nitrogen (of air) remains unaffected throughout the process. Both these reactions are endothermic. Hence the coal bed has only around 1000°C; in this zone (temperature falls).

In order to maintain the temperature of the bottom of the coal bed at about 1100°C (which is essential for the oxidation reaction) the quantity of the steam admitted along with air cannot be increased beyond a certain limit.

iii) **Pre-heating and Distillation zone:** This is the upper part of the fuel bed. In this uppermost zone of the coal bed temperature is between 400°C and 800°C.

In this zone the incoming coal fed from the top is heated by the outgoing gases and heat radiated from the reduction zone helps to distil the fuel, thereby volatile matter in the coal is now transferred to the producer gas in this zone.

Further, all the gases formed namely CO, N\(_2\), CO\(_2\), H\(_2\) etc. pass out through the outlet.

iv) **Ash zone**

The lowest zone consists mainly of ash, and therefore, it is known as ash zone.

The ash protects the plant from the intense heat of combustion. Moreover, the temperature of air and steam supplied is increased as they pass through this zone.

**Uses:**

1. The fuel is economical as it can be obtained by using even low grade coal.
2. It is used for heating open-hearth furnace, glass furnace, muffle furnace etc.
3. It can be used as reducing agent in metallurgic operation.

1.8 Water gas (or Blue gas)

Composition:

<table>
<thead>
<tr>
<th>Combustible gases</th>
<th>Non-combustible gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO = 40-42%</td>
<td>CO₂ = 3-5%</td>
</tr>
<tr>
<td>H₂ = 48-51%</td>
<td>N₂ = 3-6%</td>
</tr>
</tbody>
</table>

Calorific value: 27,800 kcals/m³

The term, „Water gas“ has been given to the mixture of combustible gases CO and H₂ because water in the form of steam is used to make this mixture of gases. Since this gas burns with a blue flame because of its high carbon monoxide content it is also known as blue gas.

Manufacture:

It is prepared by passing steam and little air through a bed hot coal (or) coke. The reaction takes place at about 900° to 1000°C

Reactions:

Water gas is prepared by reacting steam over red hot coke in a cyclic process comprising of the following two main steps:

i) Air is passed through the coke bed when carbon burns to CO₂ and the temperature of the fuel bed increases to over 1000°C

\[ C + (O₂ + N₂) \text{ Air} \rightarrow CO₂ + N₂ \text{ (exothermic)} \]

The outgoing gases containing CO₂ and N₂ are used to preheat the incoming air and steam.

ii) Steam is now blown through the red hot coke when CO and H₂ are produced. This is let out through the water gas outlet.

At higher temperatures

\[ C + H₂O \rightarrow CO + H₂ \text{ (endothermic)} \]

At lower temperatures

\[ C + 2H₂O \rightarrow CO₂ + 2H₂ \text{ (endothermic)} \]
These reactions being endothermic, the temperature of the fuel bed falls below 1000°C. At this stage, steam supply is cut off and air is again blown to raise the temperature to 1000-1100°C. Then the steam is blown in and the process is repeated. In order to maintain the temperature of the fuel bed above 1000°C, the air and steam supply are regulated alternatively to achieve the desired effects.

The period for which air is passed is called “hot blow” and that for which steam blow is usually 4 minutes while the period of air blow is very short (about 1-2 minutes). The duration of these periods are adjusted in such a way that the maximum yield of water gas is obtained.

Uses:
1. Because of its high calorific value, water gas is used as a good fuel.
2. It is a good source of hydrogen on commercial scale.
3. A mixture of water gas and producer gas is used for the manufacture of ammonia by Haber’s process.
4. Mixed with hydrogen it is used in the manufacture of methyl alcohol.
5. Used for the preparation of carbureted water gas (water gas + gaseous hydrocarbon)
6. It is also used for welding purposes.

2 COMBUSTION

Chemical combination of oxygen and fuel molecules with evolution of large amount of heat is called combustion.

Fuel + Oxygen $\rightarrow$ large amount of heat
2.1 Calorific value

It is the total quantity of heat liberated when an unit mass of the fuel is completely burnt.

2.1.1 Higher (or) Gross Calorific Value (HCV OR GCV)

Hydrogen is present in almost all fuels. When the calorific value is determined, hydrogen is converted into steam. If the products of combustion are condensed to room temperature, the latent heat of condensation of steam is also included in the measured heat. This value is called higher or gross calorific value.

The higher or gross calorific value is the total amount of heat produced when an unit quantity of the fuel is completely burnt and the products of combustion are cooled to room temperature.

2.1.2 Lower (or) Net Calorific Value (LCV OR NCV)

In actual practice the water vapours escape along with hot combustion gases. Hence, a lesser amount of heat is available. This is called lower or net calorific value.

Lower or net calorific value is defined as the net heat produced when an unit quantity of the fuel is completely burnt and the products of combustion are allowed to escape.

Relationship between higher and lower calorific values

\[ \text{NCV} = \text{Gross calorific value} – \text{latent heat of water vapour formed} \]
\[ = \text{GCV} – \text{Mass of hydrogen} \times 9 \times \text{latent heat of steam} \]
\[ = \text{GCV} – \text{Mass of hydrogen} \times 9 \times 587 \text{ kcals/kg} \]

2.1.3 Dulong’s formula

(Theoretical Calculation of Calorific Value)

The calorific value from the chemical composition of the fuel is calculated based on Dulong’s formula.

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

Where C, H, O and S are the % of Carbon, Hydrogen, Oxygen and Sulphur in the fuel.
NCV or LCV = \[ HCV - \frac{9}{100} \times H \times 587 \] kcal/kg

2.2 Simple Problem

A coal has the following composition in ultimate analysis: C=80% S=2.5% N=0.6% H=7.5% and oxygen 9.4%. Find the gross and net calorific values with the help of Dulong’s formula.

Solution:

C=80% S=2.5% H=7.5% O=9.4%.

GCV or HCV =

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

= \frac{1}{100} [8080 \times 80 + 34500(7.5 - 9.4/8) + 2240 \times 2.5]

= \frac{1}{100} [646400 + 34500(7.5 - 1.175) + 5600]

GCV = 8702 kcal/kg

NCV = [GVC – 9/100 \times H \times 587]

= [8702 - 9/100 \times 7.5 \times 587]
2.3 Calculation of theoretical oxygen and air requirement

Combustion is an exothermic chemical reaction accompanied by the increase of heat.

\[ C + O_2 \rightarrow CO_2 (g) + 97\text{Kcals} \]

The minimum quantity of air required for the complete combustion of the fuel can be calculated from the percentage composition of the fuel. The main elements present in most of the fuels are C, H, O and S.

**Combustion of carbon**

C(s) + O_2 (g) \rightarrow CO_2 (g)

\[ \begin{array}{c|c|c}
12 & 32 & 44 \\
\end{array} \]

12 kg of Carbon requires oxygen for complete combustion = 32 kg

The given carbon (C kg) in the fuel requires oxygen for complete combustion

\[ = \frac{32}{12} xC \]

**Combustion of hydrogen**

\[ 2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l) \]

\[ \begin{array}{c|c|c}
4 & 32 & 36 \\
\end{array} \]

4 kg of hydrogen requires oxygen for complete combustion = 32 kg

The given hydrogen (H kg) in the fuel required oxygen for complete combustion

\[ = \frac{32}{4} xH \text{ kg} \]

From the total amount of hydrogen in the fuel part of hydrogen are non combustible in the form of water.

8 part of oxygen combines with 1 part of hydrogen

The amount of hydrogen available for combustion

\[ = H - \frac{O}{8} \]
Oxygen required for the complete combustion of hydrogen

\[
\left(\frac{32}{4}\right)\left(\frac{H - O}{8}\right)
\]

Combustion of sulphur

\[
S(s) + O_2(g) \rightarrow SO_2(g)
\]

32 kg of sulphur required oxygen for complete combustion = 32 kg

The given sulphur in the fuel requires oxygen for complete combustion = \(\frac{32}{32}xS\) kg

On combining the above three combustion equations we get the equation for the theoretical oxygen requirement for the combustion of C, H and S.

\[
\begin{bmatrix}
\left(\frac{C + 8}{32}\right)H - \left(\frac{O}{8}\right) + S
\end{bmatrix}
\]

Minimum weight of air required for complete combustion = \(\frac{100}{23}\)

\[
\begin{bmatrix}
\left(\frac{C + 8}{32}\right)H - \left(\frac{O}{8}\right) + S
\end{bmatrix}
\]

Minimum volume of air required

\[
\begin{bmatrix}
\left(\frac{C + 8}{32}\right)H - \left(\frac{O}{8}\right) + S
\end{bmatrix}
\]

Example 1

Calculate the weight and volume of air required for the combustion of 1 kg of coal.

Solution:

According to combustion equation

\[
C(s) + O_2(g) \rightarrow CO_2(g)
\]

Weight of oxygen required by 1Kg of coal = \(\frac{32}{12}\)

= 2.667 kg of oxygen

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Air contains 23% of oxygen by weight

Weight of air required \[ = 2.667 \times (100/23) \]
\[ = 11.59 \text{ kg}. \]

**Example 2**

Calculate the minimum volume of air used for the complete combustion of a fuel having the following composition by weight.

\[ \text{C}=92\% \quad \text{H}_2=4\% \quad \text{O}_2=2\% \quad \text{ash}=2\% \]

Minimum volume of air required for combustion

\[
= \frac{100}{21} \left[ \left( \frac{C+8}{32} \right) \left( \frac{H}{12} \right) \left( \frac{O}{8} \right) \right] + S
\]
2.4 Flue gas Analysis (Orsat’s Method)

The hot gases coming out after the combustion of a fuel is called flue gas. The flue gas contains carbon monoxide, carbon dioxide, oxygen, etc.

Significance of Flue gas:

Flue gas analysis gives idea about the complete or incomplete combustion process. The presence of a high CO in the flue gas shows incomplete combustion of the fuel and also indicates the short supply of O\textsubscript{2}. If the flue gas contains a considerable amount of O\textsubscript{2} it indicates an excess supply of oxygen.

Description of Orsat’s apparatus

The Orsat apparatus consists of a horizontal tube with a three way stop-cock at one end and water jacketed measuring burette at the other end. The free end of the three way stop cock is connected to a U-tube packed with fused CaCl\textsubscript{2}. The graduated burette is surrounded by a water jacket to keep the temperature of the flue gas constant. The lower end of the burette is connected to a water reservoir by means of a rubber tube. The level of water in the water reservoir can be raising or lowering the water reservoir (Fig.4.6)

![Orsat’s apparatus image]

The central portion of the horizontal tube is connected with three different absorption bulbs A, B and C. Bulb A contains KOH solution and it absorbs CO\textsubscript{2} only. Bulb B contains alkaline pyrogallic acid (pyrogallic acid + KOH + water) to absorb CO\textsubscript{2} and O\textsubscript{2}. Bulb C contains

\[
= (100/21) \times [(32/12) \times 0.92 + 8 (0.04-0.02) + 0]
\]

=13.11m\textsuperscript{3}
ammoniacal cuprous chloride (cuprous chloride + liqour ammonia + water) and it can absorb CO₂, O₂ and CO.

**Working of Orsat’s apparatus**
Step 1

To start with, the whole apparatus is thoroughly cleaned and properly greased. The
absorption bulbs are filled with the respective solutions to level just below their rubber connections. Their stop cocks are then closed.

The three way stop cock is opened to the atmosphere and reservoir is raised till the burette is completely filled with water. This removes air present in the burette. Now the three way stop cock is connected to the flue gas supply and the reservoir is lowered to draw the flue gas in. The sample gas mixes with some air present in the apparatus. So the three way stop cock is opened to the atmosphere to expel the gas. This process is repeated 3-4 times for completely removing the air in the apparatus.

The flue gas is sucked in the burette by opening the three way stop cock and by lowering the water reservoir. The volume of the gas taken in the burette is 100 ml at atmospheric pressure. The three way stop cock is now closed.

**Step 2**

The stopper of the bulb A is opened and the gas is passed into this bulb by raising the water reservoir. CO₂ present in the flue gas is absorbed by KOH. The gas is again sent to the burette. This process is repeated several times to ensure complete absorption of CO₂. The unabsorbed gas is finally taken back to the burette by raising the liquid in the bulb A till it is filled completely. Now the stopper of bulb A is closed. The level of water in the burette and reservoir are equalized and the column of residual gas is noted. The decrease in volume gives the volume of CO₂ in 100ml of the flue gas.

**Step 3**

The quantities of O₂ and CO are similarly determined by passing the remaining gas through bulb B and C respectively. The gas remaining in burette after absorption of CO₂, O₂ and CO is taken as N₂

Percentage of N₂ = 100 - Percentage of (CO₂+O₂+CO)

**Precautions**

1. All the air in the apparatus should be completely removed.
2. It is a must to follow the order of absorbing the gases, CO₂ first, O₂ second and CO last.

2. **Ultimate analysis**

Ultimate deals with the determination of carbon, hydrogen, nitrogen, oxygen and sulphur in coal. This analysis gives exact results which are useful in calculating calorific value of coal by using Dulong formula.
i) Determination of carbon and hydrogen

Coal sample is strongly heated with dry cupric oxide in presence of dry oxygen. Carbon present is oxidized to CO$_2$ while hydrogen present is oxidized to water vapour.

\[ \begin{align*}
C + O_2 & \rightarrow CO_2 \\
H_2 + \frac{1}{2} O_2 & \rightarrow H_2O
\end{align*} \]

After complete combustion the products enter through two bulbs, one containing weighed amount of anhydrous CaCl$_2$ which absorbs water and the other containing weighed amount of KOH which absorbs CO$_2$.

When the reaction is over, the absorption apparatus is disconnected and weighed. The increase in the weight of CaCl$_2$ bulb represents the weight of water formed, while the increase in the weight of KOH bulb represents the weight of CO$_2$ formed.

Knowing the weights of these products % of carbon and % of hydrogen can be calculated.

\[
\text{Percentage of Carbon} = \frac{12}{44} \times 100 \times \frac{\text{Weight of CO}_2 \text{formed}}{\text{Weight of Coal sample}}
\]

\[
\text{Percentage of Hydrogen} = \frac{2}{18} \times 100 \times \frac{\text{Weight of H}_2\text{O formed}}{\text{Weight of Coal sample}}
\]

ii) Determination of Nitrogen (Kjeldahl’s method)

Kjeldahl’s method is used for this purpose. In this method coal is heated with conc. H$_2$SO$_4$ in the presence of K$_2$SO$_4$ and CuSO$_4$. Indirectly the whole nitrogen present in the coal sample is converted into ammonium sulphate and a clear solution is obtained. The % of nitrogen present in the coal sample can be calculated by volumetric analysis.

\[ 2N + 6H + H_2SO_4 \rightarrow (NH_4)_2SO_4 \]

The solution is then treated with 50% NaOH, so as to liberate ammonia.

\[ (NH_4)_2SO_4 + NaOH \rightarrow 2NH_3 \uparrow + Na_2SO_4 + 2H_2O \]

The liberated ammonia is then distilled over and absorbed in known quantity of std. H$_2$SO$_4$
2NH₄ + H₂SO₄ → (NH₄)₂SO₄

Unused quantity of sulphuric acid (V₂) is determined by titrating it against standard NaOH solution by back titration. A blank titration is carried out to know the volume of total sulphuric acid (V₁) in terms of standard NaOH. The difference between blank titration (V₁-V₂) gives the amount of sulphric acid used to absorb ammonia.
Calculation:

\[
\text{% of Nitrogen} = \frac{H_2SO_4 \text{ used(ml)} \times \text{Normality of acid} \times 1.4}{\text{Weight of Coal sample}}
\]

\[
\text{% of Nitrogen} = \frac{(V_1-V_2) \times \text{Normality of acid} \times 1.4}{\text{Weight of Coal sample}}
\]

iii) Determination of sulphur

During combustion sulphur in coal is converted into sulphate. It is further treated with barium chloride solution, so that sulphates are precipitated as BaSO₄.

\[\text{S} + \text{O}_2 \rightarrow \text{SO}_2 \rightarrow \text{SO}_4^{2-}\]

\[\text{SO}_4^{2-} + \text{BaCl}_2 \rightarrow \text{BaSO}_4 + 2 \text{Cl}^-\]

Knowing the weight of BaSO₄, % of sulphur present in coal sample can be calculated.

A known amount of coal is burnt completely in Bomb calorimeter in a current of oxygen. During burning, sulphur present in coal is oxidized to sulphates. Ash formed from the bomb calorimeter is extracted with dilute hydrochloric acid. Then acid extract is treated with barium chloride solution to precipitate sulphate as BaSO₄. The precipitates of BaSO₄ are filtered, washed, dried and weighed. Knowing the weight of BaSO₄, % of sulphur can be calculated.

Calculation:

If 233 gm of BaSO₄ is obtained then

sulphur present in coal = 32 gm.

(1 gm molecular weight of BaSO₄)

If \( \text{W}_2 \) gm of BaSO₄ obtained (in experiment)

then sulphur present in coal \( = \frac{32}{233} \times \text{W}_2 \)

\( \text{W} \) gm of coal sample contain \( = \frac{32}{233} \times \text{W}_2 \) of sulphur

\[\text{Percentage of Sulphur} = \frac{32}{233} \times \frac{\text{W}_2}{\text{W}} \times 100\]

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Where \[ W = \text{weight of coal taken} \]
\[ W_2 = \text{weight of BaSO}_4 \text{ formed.} \]

iv) **Determination of oxygen**

It is determined indirectly by deducting the combined percentage of C, H, N, S and ash from 100

Percentage of oxygen = 100 - (\% of C + H +N +S + ash)

Note: ash % is determined as done in proximate analysis.

**Significance of Ultimate Analysis**

<table>
<thead>
<tr>
<th>Element present in coal</th>
<th>Merits</th>
<th>Demerits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon and hydrogen</td>
<td>Calorific value of coal increases with the increase in % of carbon and hydrogen. Also the quality of coal will be better if percentage of these elements is higher.</td>
<td>Normally hydrogen present in coal sample is in the form of water. So, major portion of heat energy is wasted.</td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td>Nitrogen present in coal sample doesn’t have any calorific value because nitrogen is an inert and incombustible matter.</td>
</tr>
<tr>
<td>Sulphur</td>
<td>Sulphur increases the calorific value of coal.</td>
<td>During combustion it emits harmful gases like SO(_2), SO(_3) which causes air pollution.</td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
<td>Oxygen present in coal is in the form of water. Thus equivalent amount of hydrogen is not available for combustion and thus the calorific value accordingly decreases.</td>
</tr>
</tbody>
</table>

**14.20 Natural Gas**
Natural gas is formed by the decomposition of organic matter. The natural gas is found along with crude petroleum and coal. Compressed natural gas is known as CNG.

Natural gas is mainly composed of methane and other saturated hydrocarbons. A typical natural gas has the following compositions.

- Methane = 85% Butane = 1.5%
- Ethane = 8% Higher hydrocarbons = 1.5%
- Propane = 4% \( \text{CO}_2, \text{CO}, \text{N}_2, \text{H}_2\text{S} \) = trace levels

Trace level quantities like \( \text{CO}_2, \text{CO}, \text{N}_2, \text{H}_2\text{S} \) are removed by suitable treatment before it reaches the consumer.

If lower hydrocarbons are mainly present (methane and ethane) in natural gas then the particular natural gas is called “dry gas” (marsh gas).

If higher hydrocarbons are mainly present along with then the particular natural gas is called “wet gas”.

Natural gas is cheap as well as convenient fuel and it burns with hot blue flame.

Its calorific value is very high (12000-14000 kcal/m\(^3\)).

It is used for domestic and industrial purposes.

Natural gas is used as a raw material for the synthesis of methanol, carbon black (a filter for rubber) and formaldehyde.

6. **PETROLEUM (CRUDE OIL)**

Petroleum is a dark coloured viscous liquid found deep in earth’s crust. Chemically, it is a mixture of various types of hydrocarbons along with some oxygen, sulphur and nitrogen containing compounds.

7.1. **REFINING OF PETROLEUM**

The Crude oil as such is of little important. However, it is separated into various useful fractions by fractional distillation. This is called refining of petroleum.

(i) Separation of water (Cottrell’s process)

The crude oil is an extremely stable emulsion of oil and salt water. The crude oil
is allowed to flow through two highly charged electrodes. The colloidal water droplets coalesce to form large drops, which separate out from the oil.

(ii) Removal of harmful sulphur compounds

The oil treated with copper oxide. The copper sulphide formed is removed by filtration.

(iii) Fractional distillation

The crude oil is heated to about 400°C in and iron retort, where all volatile constituents evaporate except the asphalt residue. The hot vapours are passed into a fractionating column (buffle tower) (Fig.14.3).

7.2. Major fraction products from crude oil

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Name of fraction</th>
<th>Boiling range</th>
<th>Average composition in terms of hydrocarbons</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Uncondensed gas</td>
<td>&lt;30°C</td>
<td>Lower hydrocarbons (C_1-C_4)</td>
<td>Used as domestic industrial fuel(LPG)</td>
</tr>
<tr>
<td>2.</td>
<td>Petroleum ether</td>
<td>40-80°C</td>
<td>C_5-C_7</td>
<td>As solvent</td>
</tr>
<tr>
<td>3.</td>
<td>Gasoline</td>
<td>40-120°C</td>
<td>C_8-C_9</td>
<td>As motor and aviation fuel and for dry cleaning work</td>
</tr>
<tr>
<td>4.</td>
<td>Naptha (solvent spirit)</td>
<td>120-180°C</td>
<td>C_9-C_10</td>
<td>As solvent; as feed stock for petrochemicals</td>
</tr>
<tr>
<td>5.</td>
<td>Kerosene oil</td>
<td>180-250°C</td>
<td>C_{10}-C_{16}</td>
<td>For lighting purposes; feed stock for reforming processes.</td>
</tr>
<tr>
<td>6.</td>
<td>Diesel oil</td>
<td>250-320°C</td>
<td>C_{16}-C_{16}</td>
<td>As engine fuel</td>
</tr>
<tr>
<td>7.</td>
<td>Heavy oil</td>
<td>320-400°C</td>
<td>C_{17}-C_{30}</td>
<td>For getting gasoline by cracking</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>Lubricating oil</td>
<td>-</td>
<td>-</td>
<td>As lubricant</td>
</tr>
<tr>
<td>9.</td>
<td>Vaseline</td>
<td>-</td>
<td>-</td>
<td>In cosmetics and medicine</td>
</tr>
<tr>
<td>10.</td>
<td>Grease</td>
<td>-</td>
<td>-</td>
<td>As lubricant</td>
</tr>
<tr>
<td>11.</td>
<td>Paraffin wax</td>
<td>-</td>
<td>-</td>
<td>In candles, boot polish, tarpaulin, etc.</td>
</tr>
<tr>
<td>12.</td>
<td>Residue</td>
<td>&gt;400°C</td>
<td>C₃₀ and above</td>
<td>In road topping, water proofing of roofs. As a fuel and in moulding work (a)Asphalt (b)Petroleum</td>
</tr>
</tbody>
</table>

The fractioning column is a tall cylindrical tower containing a number of horizontal steel trays one over another of a fixed distance. Each tray is provided with small chimney covered with loose cap.

As the vapours go up, they become cooled and condensed. Higher boiling fractions condense first, while the lower boiling fractions turn-by-turn. The different fractions obtained at different trays are shown in the table 7.2

8. **CRACKING**

Cracking is defined as the decomposition of higher molecular weight hydrocarbon molecules (high b.pt) into smaller molecular weight hydrocarbon (low b.pt)

\[
\text{cracking} \\
C_{10}H_{22} \rightarrow C_{5}H_{10} + C_{5}H_{12}
\]

Decane \hspace{1cm} n-pentene \hspace{1cm} n-pentane

B.pt=174°C \hspace{1cm} B.pt=36°C

There are two methods of cracking

8.1 **THERMAL CRACKING**

Cracking is carried out by the application of heat and pressure is known as thermal cracking. Here the bigger hydrocarbon molecules break down to give smaller molecules of alkanes, alkenes and some hydrogen.

Thermal cracking may be carried out either in liquid phase or in vapour phase.
a. Liquid phase thermal cracking

The heavy oil is cracked at a temperature of 475-530°C and pressure of about 100 kg/cm. The cracked products are then separated in a fractioning column.

The yield is 50-60% and octane rating of petrol is 65-70%

b. Vapour phase thermal cracking

This type of cracking is suitable for oils which may be readily vapourised. The crude oil is first vapourised and then cracked at about 600-650°C. Petrol obtained has better antiknocking properties.

8.2 CATALYTIC CRACKING
Cracking is carried out using a catalyst is known as catalytic cracking. The catalyst used is aluminium silicate or alumina.

8.3 ADVANTAGES OF CATALYTIC CRACKING
1. The yield of petrol is higher
2. The quality of petrol is better
3. A much lower pressure is needed
4. The cracking process can be controlled
5. No external fuel is necessary for cracking
6. The product contains very little amount of undesirable products.
7. The percentage of gum and gum forming compounds are low.
8. Catalysts are selective in their action, and therefore cracking of higher boiling hydrocarbon takes place.
9. The product contains a higher amount of aromatic and hence better antiknocking property.

8.4. CATALYTIC CRACKING METHODS
There are two types of methods for catalytic cracking

a. Fixed bed catalytic cracking
b. Moving bed or Fluid bed catalytic cracking

8.4.1. Fixed bed catalytic cracking
The heavy oil fraction is heated in a particular in a preheater at a temperature of 420-450°C. The vapours are then forced into a catalytic chamber containing artificial clay mixed with zirconium oxide. The temperature of the chamber is 425-450°C and pressure is 1.5 kg/cm. cracking of the oil takes place. About 40% of the charge is converted into gasoline and about 2-4% carbon is formed. This carbon gets deposited over the catalyst bed. The cracked vapours are then passed into a fractionating column. The gasoline vapours and other gaseous products are obtained from the top, while the heavy oil condenses at the bottom. These vapours are passed into a cooler where gasoline is condensed along with some gaseous products. The gasoline containing some dissolved
gases is sent to a stabilizer, where the dissolved gases are removed and pure gasoline is obtained.

Due to the deposition of carbon black over the catalyst bed, the catalyst stops functioning after 8-10 hours. This is reactivated by burning off the deposited carbon.

8.4.2. Moving bed (or) Fluid bed catalytic cracking
The solid catalyst is very finely powdered, so that it behaves as a fluid, which can be circulated in gas stream.

The vapours of the gas oil or heavy oil mixed with fluidized catalyst are forced up into a large reactor maintained at 500°C. The cracking of heavier into lighter molecule occurs. There is a centrifugal separator (cyclone) near the top of the reactor which allows only the cracked vapours to pass on to the fractioning column, but retains the carbon powders in the reactor itself. The gasoline vapours and other gaseous products are obtained from the top of the fractioning column. These vapours are passed into a cooler where gasoline is condensed along with some gaseous products. The gasoline containing some dissolved gases is sent to stabilizer, where the dissolved gases are removed and pure gasoline is obtained (Fig.14.5).

Due to coating of carbon the catalyst gets heavier gradually and settles down at the bottom. This spent catalyst is then pumped by air stream to another chamber known as regenerator. In the regenerator, carbon is burnt and CO pass out through the regenerated cyclone resperator at the top of the chamber. Catalyst then flows through a stand-pipe for mixing with a fresh charge.