INTRODUCTION

A fuel is a combustible substance containing carbon as the main constituent which on proper burning gives large amount of heat that can be used economically for domestic and industrial 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.

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

So, 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.

Classification of Fuels are classified as

1. Primary fuels which occur in nature as such, e.g. coal, petroleum and natural gas.
2. Secondary fuels which are derived from the primary fuels, e.g. coke, gasoline, coal gas, etc.

Both primary and secondary fuels may be further classified based upon their physical state as (i) solid fuels (ii) liquid fuels and (iii) gaseous fuels.

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. It 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 cal

(3) "British Thermal unit" (B.T.U.) 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 B.T.U. = 252 cal = 0.252 kcal
1 kcal = 3.968 B.T.U.

Higher or gross calorific value (HCV)

Higher or gross calorific value: Usually, 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 (15°C or 60°F), the latent heat of condensation of steam also gets included in the measured heat, which is then called "higher or gross calorific value". So, gross or higher calorific value (HCV) 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" (i.e., 15°C or 60°F).

**Lower or net calorific value (LCV)**

Lower or net calorific value: In actual use 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. So, net or lower calorific value (LCV) is "the net heat produced, when unit mass /volume of the fuel is burnt completely and the products are permitted to escape".

Net calorific value = Gross calorific value - Latent heat of condensation of water vapour produced
= GCV - Mass of hydrogen per unit weight of the fuel burnt x 9 x Latent heat of condensation of water vapour

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

\[
\text{HCV} = \frac{1}{100} \left[ 8,080 \, C + 34,500 \left( H - \frac{O}{8} \right) + 2,240 \, S \right] \text{kcal/kg}
\]

where C, H, O, and S are the percentages of carbon, hydrogen, oxygen and sulphur in the fuel respectively. In this formula, oxygen is assumed to be present in combination with hydrogen as water, and

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

This is based on the fact that 1 part of H by mass gives 9 parts of H₂O, and latent heat of steam is 587 kcal/kg.
Solid fuel- Coal- classifications, Analysis- Proximate and ultimate

COAL

Coal is regarded as a fossil fuel produced from large accumulations of vegetable debris due to partial decay and alteration by the action of heat and pressure over millions of years. Coal is a highly carbonaceous matter that has been formed as a result of alteration of vegetable matter (e.g., plants) under certain favourable conditions. It is chiefly composed of C, H, N, and O, besides non-combustible inorganic matter.

Classification of Coal

Coals are classified on the basis of their rank. Rank is defined as the degree or extent of maturation and is therefore a qualitative measure of carbon contents. Peat, lignite and sub-bituminous coals are referred as low rank coals while bituminous coals and anthracites are classed as high rank. In European terminology, the lignite and sub-bituminous coals are called soft coals while bituminous coals and anthracite coals are termed as hard coals. In North American terminology, the coal series is written as

Wood → peat → lignite → bituminous → anthracite.

Analysis of Coal

In order to assess the quality of coal the following two types of analysis are made.

1. **Proximate Analysis** It includes the determination of moisture, volatile matter, ash and fixed carbon. This gives quick and valuable information regarding commercial classification and determination of suitability for a particular industrial use.

2. **Ultimate Analysis** It includes the determination of carbon, hydrogen, nitrogen, sulphur and oxygen in coal. Since it is used for the determination of elements present in the coal, it is also called elemental analysis. This analysis gives exact results and are useful in calculating the calorific value of coal using Dulong’s formula.

(1) **Proximate analysis**

1. **Moisture:** About 1 g of finely powered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105° - 110°C. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in a desiccator and weighed. Loss in weight is reported as moisture (on percentage-basis).

   \[
   \text{Percentage of moisture} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100
   \]

2. **Volatile matter:** The dried sample of coal left in the crucible in (1) is then covered with a lid and placed in an electric furnace (muffle furnace), maintained at 925°± 20°C. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside a desiccator and
weighed again. Loss in weight is reported as volatile matter on percentage-basis.

\[
\text{Percentage of volatile matter} = \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Wt. of coal sample taken}} \times 100
\]

(3) **Ash:** The residual coal in the crucible in (2) is then heated without lid in a muffle furnace at 700 ± 50°C for 1/2 hour. The crucible is then taken out, cooled first in air, then in desiccator and weighed. Heating, cooling and weighing is repeated, till a *constant weight* is obtained. The residue is reported as ash on percentage-basis.

\[
\text{Percentage of ash} = \frac{\text{Wt. of ash left}}{\text{Wt. of coal taken}} \times 100
\]

(4) **Fixed carbon:** Percentage of fixed carbon = 100 - % of (moisture + volatile matter + ash)

**Importance of proximate analysis:**

Proximate analysis provides following valuable informations in assessing the *quality of coal*:

(1) **Moisture:** Moisture lowers the effective calorific value of coal. Moreover, 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 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. Higher volatile content in coal is undesirable. A high volatile matter content means that high-proportion of fuel will be distilled and burned as a gas or vapour. The volatile matter present in the coal may be combustible gases (such as methane, hydrogen, carbon monoxide and other hydrocarbons) or non-combustible gases (like CO₂ and N₂). Volatile matter content is of special significance in coal gas manufacture and in carbonization plants, particularly when by-product recovery is the main object. Thus, high-volatile matter containing coals do not cake well; whereas medium-volatile matter content coals are capable of yielding hard and strong coke on carbonization.

(3) **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 clinker), which block the inters paces of the grate. 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. 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 (in coal) that can be burnt by a primary current of air drawn through the hot bed of a fuel. Hence, high percentage of rued carbon is desirable.

**B** **Ultimate analysis** involves in the following determinations:

(1) **Carbon and hydrogen:** About 1-2 g 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 CO₂ and H₂O
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.

\[
\begin{align*}
\text{C} + \text{O}_2 & \rightarrow \text{CO}_2 + \frac{1}{2}\text{H}_2\text{O} \\
12 & \quad 44 & \quad 2 & \quad 18
\end{align*}
\]

\[
\begin{align*}
2 \text{KOH} + \text{CO}_2 & \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \\
\text{CaCl}_2 + 7 \text{H}_2\text{O} & \rightarrow \text{CaCl}_2 \cdot 7 \text{H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{Percentage of C} = & \quad \frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{Weight of coal sample taken} \times 44} \\
\text{and percentage of H} = & \quad \frac{\text{Increase in weight of CaCl}_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal sample taken} \times 18}
\end{align*}
\]

\(\text{(2) Nitrogen:}\) About 1 g of accurately weighed powdered coal is heated with concentrated H\(_2\)SO\(_4\) along-with K\(_2\)SO\(_4\)(catalyst) in a long-necked flask(called 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:

\[
\begin{align*}
\text{Percentage of N} = & \quad \frac{\text{Volume of acid used} \times \text{Normality} \times 1.4}{\text{Weight of coal taken}}
\end{align*}
\]

\(\text{(3) Sulphur}\) is determined from the washings obtained from the known mass of coal, used in a 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.

\[
\begin{align*}
\text{Percentage of S} = & \quad \frac{\text{Weight of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{Weight of coal sample taken in bomb} \times 233}
\end{align*}
\]

(4) Ash determination is carried out as in proximate analysis.

(5) Oxygen: It is obtained by difference.

\[
\begin{align*}
\text{Percentage of O} = 100 - \text{Percentage of (C + H + S + N + ash)}
\end{align*}
\]

**Significance of ultimate analysis:**

\(\text{(1) Carbon and hydrogen:}\) 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. Also higher percentage of carbon in coal reduces the size of combustion chamber required. The amount of carbon, the major combustible constituent of coal, depends on the type of coal and its percentage increases with rank from lignite to anthracite. Thus, percentage of carbon forms the basis of classification of coal.
(2) **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**, although contributes to the heating value of coal, yet on combustion produces acids (SO$_2$ and 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 3.0% 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 (formed as combustion products) pollute the atmosphere and leads to corrosion.

(4) **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 in 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.
Carbonization process-Metallurgical coke-Manufacture of coke by Otto Hoffmann process.

**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 SO$_2$, P$_2$O$_3$ and P$_2$O$_5$, 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$^\circ$ - 900$^\circ$C), all cokes appears to be equally reactive. At about 1,000$^\circ$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.

**Coal versus coke in metallurgical processes**:

1. Coal does not possess as much strength and porosity as coke.
2. By coking, much of undesirable sulphur is removed.
3. Coke burns with short flame, due to expulsion of much of its volatile matter during carbonization.

Because of these reasons, "coke is preferred to coal for metallurgical purposes", particularly in blast
furnaces. On the other hand, coal burns with a long flame, which is suitable only for reverberatory furnaces.

Coking quality: The coals which on heating, in the absence of air, becomes soft, plastic and together to large coherent masses, are called caking coals. Consequently, such coals are difficult to be oxidized. If the residue (i.e.: coke) obtained after heating is porous, hard, strong and usable for metallurgical purpose, the original coal, is known as coking coal.

**TYPES OF CARBONIZATION OF COAL**

These are two 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 by-product 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** 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**

The coke, for *metallurgical purposes*, is obtained by either of the following processes:

**Otto Hoffman’s by-product oven:**

In order to: (1) increase the thermal efficiency of the carbonization process, and (ii) recover valuable by-product (like coal gas, ammonia, benzol oil, tar, etc.), Otto Hoffman developed modern by-product coke oven which, unlike beehive oven, is heated externally by a portion of coal gas produced during the process itself or by producer gas or by blast furnace gas. Moreover, the heating is done on the basis of "regenerative system of heat economy", i.e., utilizing the waste flue gases for heating the checker-work of bricks.

The by-product coke oven consists of number of narrow *silica chambers* (each about 10 to 12 m long, 3 to 4 m high and 0.40 to 0.45 m wide) erected side-by-side with *vertical flues* in-between them to form a sort of battery. Each chamber is provided with a *charging hole at the top*, a *gas off-take* and a *refractory-lined cast iron door* at each ends for discharging coke.

A charge consisting of *finely crushed coal* is introduced through the charging holes at the top of chambers, which are then closed tightly at both ends to prevent any access of air. The coke ovens are heated to 1,200°C by burning gaseous fuel (like producer gas) and usually employing a regenerative principle to achieve as economical heating as possible. The flue gases produced during combustion, before escaping to chimney, pass on their *sensible heat* to one of the two sets of checker brick-work, until this brick-work has been raised to a temperature of about 1,000°C. The flow of heating gases is then reversed and the inlet gases are
Otto Hoffman's by-product oven passed through the heated checker brick-work, which thus serves to preheat the inlet gases. The flue gases are then allowed to pass through the second set of checker bricks to heat it. This checker-work then serves to preheat the inlet gases. Thus, this cycle goes on. The heating is actually continued, till the evolution of volatile matter ceases completely. Carbonization of a charge of coal takes about between 11 to 18 hours. When carbonization is completed, a massive ram pushes the red hot coke into a truck. It is subsequently quenched by a water spray (‘wet quenching’). In place of wet quenching, "dry quenching" offers advantages, because the coke produced is more strong, dense, graphitized and non-reactive. In this method, the red hot coke is placed in a chamber and cooled by passing inert gases from boilers (like nitrogen). The heated inert gases are then circulated to boilers, where they generate steam. The coke produced by ‘dry quenching’ is cheaper, drier and contains lesser dust than 'wet-quenched' coke.

**Recovery of by-products**: The gas coming out from the oven is known as "coke oven gas" and is mainly composed of ammonia, H₂S, naphthalene, benzene, tar, moisture, etc.

(i) **Recovery of tar**: The gas is first passed through a tower in which liquor ammonia is sprayed. Here dust and tar get collected in a tank below, which is heated by steam coils to recover back ammonia sprayed. The ammonia is used again.

(ii) **Recovery of ammonia**: The gases from the chamber are then passed through a tower in which water is sprayed. Here ammonia goes into solution as NH₄OH.

(iii) **Recovery of naphthalene**: The gases are then passed through another tower in which water at very low temperature is sprayed. Here naphthalene gets condensed.

(iv) **Recovery of benzene**: The gases are then sprayed with petroleum, when benzene and its homologues are removed.

(v) **Recovery of H₂S**: The gases are then passed through a purifier, packed with moist Fe₂O₃. Here H₂S is retained.

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

After some time, when all Fe₂S₃ is changed into Fe₂O₃, the purifier is exposed to atmosphere, when Fe₂O₃ is regenerated,

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

\[
4\text{FeO} + \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3
\]
Liquid fuel-Petroleum processing and fractions-manufacture of synthetic petrol by Bergius process. Knocking in SI and CI engines. Octane and cetane number

Liquid Fuels

The important liquid fuels are petroleum, petroleum products, tar, alcohols. These are naturally found under the sea surface. Liquid fuels are also obtained synthetically from hydrogenation of coat. Liquid fuels find extensive use in domestic and industrial fields.

Petroleum

Petroleum or crude oil is a dark greenish brown or black coloured viscous oil found deep in earth's crust. The oil is usually floating over a brine solution and above the oil, natural gas is present. Crude oil containing mixture of paraffinic, olefinic and aromatic hydrocarbons with minor amounts of organic compounds like N, O and S. The average composition of crude oil is C =80 - 87 %, H =11-15%, S = 0.1 -3.5%, (N +O) =0.1- 0.5%.

a) Classification of petroleum

Petroleum is classified into three types based on variation of chemical nature of crude oil found in the earth.

i) Paraffinic-base type crude oil: It contains saturated hydrocarbons from CH$_4$ to C$_{35}$H$_{72}$ and little amount of naphthalenes and aromatics.

ii) Asphaltic-base type crude oil: It contains mainly cycloparaffins or naphthalenes with smaller amount of paraffins and aromatic hydrocarbons.

iii) Mixed-base type crude oil : It contains both paraffinic and asphaltic hydrocarbons and are generally in the form of semi-solid waxes.

Mining of Petroleum

Refining of Petroleum

The crude oil obtained from the earth crust contains water, sulphur and some unwanted impurities. After removal of water, sulphur and these impurities, the crude oil is separated into various useful fractions by fractional distillation and finally convolved into desired specific products having different boiling points. The process is called "Refining of Petroleum" and the refining plants are called "Oil refineries". The process of refining involves the following steps.

Step -I: Separation of water (Cottrell's process)

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

Step - II: Removal of harmful impurities
a) The presence of NaCl and MgCl in the crude oil can corrode the refining equipment, hence these salts are removed by electrical desalting and dehydration methods.

b) The sulphur compounds present in the crude oil is removed by treating oil with copper oxide, which results in the formation of copper sulphide (solid), which is then removed by filtration.

Step - III: Fractional distillation

The crude oil is then heated to about 400°C in an iron retort, whereby all volatile substances (except asphalt or coke) are evaporated. The hot vapors are then passed up a fractionating column, which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney covered with a loose cap. (Figure)

Fractional distillation of Crude oil

When the vapours of the oil go up in the fractionating column, they become gradually cooler and get condensed at different heights of column. The fractions having higher boiling points condense at lower trays whereas the fractions having lower boiling points condense at higher trays. The gasoline obtained by the fractional distillation is called straight --run gasoline. Various fractions obtained at different trays are given in table.
### Various fractions of crude oil and their compositions and uses

<table>
<thead>
<tr>
<th>Sn.</th>
<th>Name of the fractions</th>
<th>Boiling range (°C)</th>
<th>Composition of Hydrocarbons</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Uncondensed gases</td>
<td>Below 30°C</td>
<td>$C_1$ to $C_4$</td>
<td>As domestic and industrial fuel under the name LPG</td>
</tr>
<tr>
<td>2.</td>
<td>Petroleum ether</td>
<td>30 70 °C</td>
<td>$C_5$ to $C_7$</td>
<td>As a solvent.</td>
</tr>
<tr>
<td>3.</td>
<td>Gasoline (or) petrol.</td>
<td>40 - 120 °C</td>
<td>$C_5$ to $C_9$</td>
<td>As motor fuel, solvent and in dry cleaning.</td>
</tr>
<tr>
<td>4.</td>
<td>Naphtha (or) solvent spirit</td>
<td>120. - 180 °C</td>
<td>$C_9$ to $C_{10}$</td>
<td>As solvent and in dry cleaning.</td>
</tr>
<tr>
<td>5.</td>
<td>Kerosene oil.</td>
<td>180 - 250 °C</td>
<td>$C_{10}$ to $C_{16}$</td>
<td>As fuel for jet engines and an illuminant.</td>
</tr>
<tr>
<td>6.</td>
<td>Diesel oil (or) gas oil</td>
<td>250 320 °C</td>
<td>$C_{10}$ to $C_{18}$</td>
<td>As Diesel engine fuel.</td>
</tr>
<tr>
<td>7.</td>
<td>Heavy oil.</td>
<td>320 - 400 °C</td>
<td>$C_{17}$ to $C_{30}$</td>
<td>Production of gasoline by cracking process.</td>
</tr>
</tbody>
</table>

### Various fractions recovered from Heavy Oil

<table>
<thead>
<tr>
<th>Sn.</th>
<th>Name of the fractions</th>
<th>Boiling range (°C)</th>
<th>Composition of Hydrocarbons</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Lubricating oil</td>
<td>-</td>
<td>$C_{17}$ to $C_{20}$</td>
<td>Used as lubricants</td>
</tr>
<tr>
<td>2.</td>
<td>Petroleum jelly (Vaseline)</td>
<td>-</td>
<td>-</td>
<td>Used in medicines and cosmetics</td>
</tr>
<tr>
<td>3.</td>
<td>Paraffin wax</td>
<td>-</td>
<td>$C_{20}$ to $C_{28}$</td>
<td>Used in candles, wax paper, boot polish, etc</td>
</tr>
<tr>
<td>4.</td>
<td>Grease</td>
<td>-</td>
<td>-</td>
<td>Used as lubricants.</td>
</tr>
<tr>
<td>5.</td>
<td>Asphalt or bitumen</td>
<td>Above 400°C</td>
<td>$C_{30}$ and above</td>
<td>Used for making roads, water proof roofing, etc</td>
</tr>
</tbody>
</table>

**Cracking**

The decomposition of bigger hydrocarbon molecules into simpler, low boiling hydrocarbons of lower molecular weight is called cracking.

The gasoline obtained from the fractional distillation of petroleum, has the highest demand as a
motor fuel, but the yield of this fractions is only 20-30% (Crude oil) and also quality as straight-run gasoline which is not good an_ hence is used only after proper blending. To overcome these difficulties, the higher boiling fractions (e.g. fuel oil and gas oil) are converted into lower boiling fractions gasoline (petrol) by cracking process.

The cracked gasoline gives better engine performance i.e., they are suitable for spark-ignition engines of automobiles. In cracking process, higher saturated hydrocarbon molecules are converted into simpler molecules such as paraffinic and olefinic hydrocarbons.

There are two methods of cracking in use
1. Thermal cracking
2. Catalytic cracking

**Thermal cracking**

In this process, the heavy oil is subjected to high temperature and pressure, when the bigger hydrocarbon molecules break down to give smaller molecules of the paraffins, olefins and hydrogen. The cracked products are then separated by fractional distillation. This process is carried out in liquid phase at a temperature of 4 75 - 530° C and under pressure of 100 kg/cm$^2$ is called Liquid-phase thermal cracking or at a temperature of 600-650°C (heavy oil is vapourised) and under a low pressure of 10-20 kg/cm$^2$, such process is called Vapour-phase thermal cracking.

**Catalytic cracking**

In this process, cracking is carried out in presence of a catalyst at lower temperature (300° C to 450° C) and pressures (1 to 5 kg/cm$^2$). The catalyst like aluminium silicate [Al$_4$(SiO$_3$)] or alumina [Al$_2$O$_3$] used in cracking gives higher yield and better quality of gasoline. There are two types of catalytic cracking in use.

i) Fixed-bed catalytic cracking

The heavy oil is passed through the heater, where the oil is vapourised and heated to 400 to 500°C and then forced through a catalytic champers containing the catalyst of silica alumina gel (SiO$_2$, Al$_2$O$_3$) or bauxite, is mixed with clay and zirconium oxide maintained at 400 to 500°C and 1.5 kg/cm$^2$ pressure. During their passage through the tower, cracking takes place about 30-40% of the charge is converted into gasoline and about 2-4% carbon is formed which gets deposited on the catalytic bed. (Figure)
The vapours produced are then passed through a fractionating column, where heavy oil fractions condensed. The vapours are then admitted into a cooler, where some of the gaseous products 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.

When substantial amount of carbon is deposited on the catalyst bed, during cracking, the catalyst stops functioning. It is reactivated by burning off the deposited carbon in a stream of hot air. During the reactivation of catalyst, the vapours are diverted through another catalyst chamber.

ii) Fluid (Moving)-bed catalytic cracking

In this process, solid catalyst is finely powdered, so that it behaves almost as a fluid, which can be circulated in gas stream. The vapours of cracking stock (gas oil, heavy oil, etc.,) mixed with fluidized catalyst is forced up into a large reactor bed in which cracking of the heavier molecules into lighter molecules occurs at a temperature of 530°C and pressure of about 3' to 5 kg/cm$^2$. The top of the reactor, there is a centrifugal separator, which, allows the low boiling lighter molecules move up to the top of the reactor and enter into the fractionating column but retains all the catalyst powder in the reactor itself. The carbon deposited on the catalyst powder are burnt off in the regenerator and the temperature rises to about 590°C or more. The cracked gases and gasoline are removed from the top of the fractionating column and sent to a cooler, where gasoline is condensed. It is then sent to a stabilizer to recover pure gasoline. The product contains a higher proportion of aromatics and iso-paraffins.

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.

\[ n \text{CO} + 2n \text{H}_2 \rightarrow C_n\text{H}_{2n} + n \text{H}_2\text{O} \]

\[ n \text{CO} + (2n + 1) \text{H}_2 \rightarrow C_n\text{H}_{2n+2} + n \text{H}_2\text{O} \]

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.

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.

**Bergius process**

![Bergius process diagram]

**Knocking**

Knocking is a kind of explosion due to rapid pressure rise occurring in an IC engine. Causes of knocking in S.I Engine [Petrol engines]

In a petrol engine, a mixture of gasoline vapour and air at 1: 17 ratio is used as fuel. This mixture is compressed and ignited by an electric spark. The products of oxidation reaction (combustion) increases the pressure and pushes the piston down the cylinder. If the combustion proceeds in a regular way, there is no problem in knocking. But in some cases, the rate of combustion (oxidation) will not be uniform due to unwanted chemical constituents of gasoline. The rate of ignition of the fuel gradually increases and the final portion of the fuel-air mixture gets ignited instantaneously producing an explosive sound known as "Knocking". Knocking property of the fuel reduces the efficiency of engine. So a good gasoline should resist knocking.

**Chemical structure and knocking**

The knocking tendency of fuel hydrocarbons mainly depends on their chemical structures. The knocking tendency decreases in the following order.

Straight chain paraffins > Branched chain paraffins > Cycloparaffins > Olefins > Aromatics.

**Improvement of antiknock characteristics**

The octane number of fuel can be improved by

(i) blending petrol of high octane number with petrol of low octane number, so that the octane number of the latter can be improved.

(ii) the addition of anti-knock agents like Tetra-Ethyl Lead (TEL).
LEADED PETROL (ANTI-KNOCK AGENT)

The anti-knock properties of a gasoline can be improved by the addition of suitable additives. Tetraethyl lead (TEL) or \((C_2H_5)_4\) Pb is an important additive added to petrol. Thus the petrol containing tetra ethyl lead is called leaded petrol.

TEL reduces the knocking tendency of hydrocarbon. Knocking follows a free radical mechanism, leading to a chain growth which results in an explosion. If the chains are terminated before their growth, knocking will cease. TEL decomposes thermally to form ethyl free radicals which combine with the growing free radicals of knocking process and thus the chain growth is stopped.

Disadvantages of using TEL

When the leaded petrol is used as a fuel, the TEL is converted to lead oxide and metallic lead. This lead deposits on the spark plug and on cylinder walls which is harmful to engine life. To avoid this, small amount of ethylene dibromide is added along with TEL. This ethylene dibromide reacts with Pb and PbO to give volatile lead bromide, which goes out along with exhaust gases.

But this creates atmospheric pollution. So nowadays aromatic phosphates are used instead of TEL.

(iii) Nowadays aromatic phosphates are used as antiknock agent because it avoids lead pollution.

OCTANE NUMBER (or) OCTANE RATING

Octane number is introduced to express the knocking characteristics of petrol. It has been found that n-heptane knocks very badly and hence, its anti-knock value has been given zero. On the other hand, iso-octane gives very little knocking and so, its anti-knock value has been given 100.

Thus octane number is defined as 'the percentage of iso-octane present in a mixture of iso-octane and n-heptane.'

\[
\begin{align*}
CH_3 & \quad CH_3 \\
CH - CH_2 - C - CH_3 & \quad CH_3 \\
CH_3 & \quad CH_3
\end{align*}
\]

Iso-octane (Octane number = 100)

\[CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3\]

n - heptane (Octane number = 0)

CETANE NUMBER (or) CETANE RATING

Cetane number is introduced to express the knocking characteristics of diesel. Cetane has a very short ignition lag and hence its cetane number is taken as 100. On the other hand 2-methyl naphthalene has a long ignition lag and hence its cetane number is taken as zero.
Thus the cetane number is defined as "the percentage of hexa decane present in a mixture of hexa decane and 2-methyl napthalene, which has the same ignition lag as the fuel under test".

The cetane number decreases in the following order.

n-alkanes > Cycloalkanes > alkenes > branched alkanes > aromatics

The cetane number of a diesel oil can be increased by adding additives called dopes.

**Important** dopes: Ethyl nitrate, Iso-amyl nitrate.
Lecture 41  Gaseous fuels - CNG, LPG, Water gas and a producer gas

**COMPRESSED NATURAL GAS**

Natural Gas is obtained from wells dug in the oil bearing regions. When natural gas occurs along with petroleum in oil wells, it is called as ‘wet gas’ and contains gaseous hydrocarbons from C1 to C4. The wet gas is then suitably treated to remove propane, propene, butane and butane, which is used as LPG. When the natural gas is compressed, it is called Compressed Natural Gas (CNG). The primary component present in CNG is methane. It is mainly derived from natural gas.

The natural gas can either be stored in a tank of a vehicle as compressed natural gas (CNG) at 3,000 or 3,600 psi or as liquified natural gas (LNG) at typically 20-150 psi. A suitably designed natural gas engine may have a higher output compared with a petrol engine because the octane number of natural gas is higher than that of petrol.

Compressed natural gas vehicles require a greater amount of space for fuel storage than convention gasoline power vehicles. Since it is a compressed gas, rather than a liquid like gasoline, CNG takes up more space for each GGE (Gallon of Gas Equivalent). This makes it difficult to design smaller vehicles that look and operate like the vehicles that people are accustomed to. CNG is often confused with liquefied natural gas (LNG). While both are stored forms of natural gas, the key difference is that CNG is in compressed form, while LNG is in liquefied form. CNG has a lower cost of production and storage compared to LNG as it does not require an expensive cooling process and cryogenic tanks. CNG requires a much larger volume to store the same mass of natural gas and the use of very high pressures (3000 to 4000 lbf/in², or 205 to 275 bar).

CNG has been made mandatory for all public transport in the Indian capital city of New Delhi.

(CNG)

Properties
1. CNG is; the cheapest, cleanest and least environmentally impacting alternative fuel.
2. Vehicles powered by CNG produce less carbon monoxide and hydrocarbon (HC) emission.
3. It is less expensive than petrol and diesel.
4. The ignition temperature of CNG is about 550°C. CNG requires more air for ignition.

**Producer Gas**

Producer gas is a mixture of combustible gases, CO(30%) and H2(15%) with large amount of non combustible gases N2(56%) and CO2(3%). Its calorific value is 1300kcal/m3

It is prepared by passing air mixed with a little steam over a red hot coke maintained at about 1100°C in a special reactor called gas producer. It consists of a steel vessel of (3 m in diameter, 4f m in height) inside lined with refractory bricks. It is provided with cup and cone feeder at the top and a side opening for produced gas exit. At the bottom, it has inlets for passing air and steam.
Manufacture of producer gas

Various Reactions

The reactions of producer gas production can be divided into four zones as follows.

(i) Ash Zone
   This is the lowest zone consists mainly of ash. The incoming air and steam mixture is preheated in this zone.

(ii) Combustion or Oxidation Zone
   This is the zone next to ash zone. Here the coke is oxidised to CO and CO2. Both the reactions are exothermic. Hence, the temperature of the bed reaches around 1,100°C.

   \[
   \begin{align*}
   C + O_2 & \rightarrow CO \quad \text{exothermic} \quad H + 95 \text{ k cal} \\
   C + \frac{1}{2}O_2 & \rightarrow CO_2 \quad \text{exothermic} \quad H + 29 \text{ k cal}
   \end{align*}
   \]

(iii) Reduction Zone
   This is the middle zone. Here both CO2 and steam combine with red hot coke and liberate H2 and CO. The reduction reactions are endothermic and the temperature in the zone is about 1000°C. If no steam is supplied, the temperature of the producer raise and this may fuse the ash and refractory lining.

   \[
   \begin{align*}
   C + CO_2 & \rightarrow 2CO \quad \text{endothermic} \quad 36 \text{ k cal} \\
   C + H_2O & \rightarrow CO + H_2 \quad \text{endothermic} \quad 29 \text{ k cal}
   \end{align*}
   \]

(iv) Distillation or Drying Zone
   In this zone (400 - 800°C) the down coming coal is heated by the outgoing gases. The heat given by the gases and the heat coming out from the reduction zone will distill the fuel.
Uses
1. It is used as a reducing agent in metallurgical operations.
2. It is also used for heating muffle furnaces, open-hearth furnaces etc.

WATER GAS

It is a mixture of combustible gases, CO(41%) and H$_2$(51%) with small amount of noncombustible gases, CO$_2$(4%) and N$_2$(4%). Its calorific value is about 2800 kcal/m$^3$

Manufacture

The water gas producer consists of a tall steel vessel, lined inside with refractory bricks. It is provided with cup and cone feeder at the top and a side opening for water gas exit. At the bottom it is provided with two inlet pipes for passing air and steam.

When steam and little air is passed alternatively over a red hot coke maintained at about 900 - 1000°C in a reactor, water gas is produced.

Reactions

The reactions of water gas production involves the following two steps.

**Step 1**
In the first step, steam is passed through the red hot coke, where CO & H$_2$ gases are produced. The reaction is endothermic. Hence, the temperature of the coke bed falls.

\[ C + H_2O \rightarrow CO + H_2 \text{ endothermic } 29 \text{ k cal} \]

**Step 2**
In the second step, in order to raise the temperature of the coke bed to 1000°C, the steam supply is temporarily cut off and air is blown in. The reaction is exothermic.
Thus the steam–run and air blow are repeated alternatively to maintain proper temperature.

**Uses.**

It is used for the production of \( \text{H}_2 \) and in the synthesis of ammonia. It is also used as a source of and illuminating gas and fuel gas.
Lecture : 42 Power alcohol and Biodiesel

When ethyl alcohol is used as fuel in internal combustion engine, it is called as "power alcohol". Generally ethyl 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 absorbing 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 alcohol contains 'O' atoms, the amount of air require for complete combustion of power alcohol is lesser and therefore carburettor and engine need to be modified, when only ethyl alcohol is used as fuel.

Production of ethanol

The basic steps for large scale production of ethanol are: microbial (yeast) fermentation of sugars, distillation, dehydration (requirements vary, see Ethanol fuel mixtures, below), and denaturing. Prior to fermentation, some crops require saccharification or hydrolysis of carbohydrates such as cellulose and starch into sugars. Saccharification of cellulose is called cellulolysis. Enzymes are used to convert starch into sugar.
**Fermentation**

Ethanol is produced by microbial fermentation of the sugar. Microbial fermentation will currently only work directly with sugars. Two major components of plants, starch and cellulose, are both made up of sugars, and can in principle be converted to sugars for fermentation. Currently, only the sugar (e.g. sugar cane) and starch (e.g. corn) portions can be economically converted. There is much activity in the area of cellulosic ethanol, where the cellulose part of a plant is broken down to sugars and subsequently converted to ethanol.

**Distillation**

For the ethanol to be usable as a fuel, the majority of the water must be removed. Most of the water is removed by distillation, but the purity is limited to 95–96% due to the formation of a low-boiling water-ethanol azeotrope with maximum (95.6% m/m (96.5% v/v) ethanol and 4.4% m/m (3.5% v/v) water). This mixture is called hydrous ethanol and can be used as a fuel alone, but unlike anhydrous ethanol, hydrous ethanol is not miscible in all ratios with gasoline, so the water fraction is typically removed in further treatment in order to burn in combination with gasoline in gasoline engines.

**Dehydration**

There are basically three dehydration processes to remove the water from an azeotropic ethanol/water mixture. The first process, used in many early fuel ethanol plants, is called azeotropic distillation and consists of adding benzene or cyclohexane to the mixture. When these components are added to the mixture, it forms a heterogeneous azeotropic mixture in vapor-liquid-liquid equilibrium, which when distilled produces anhydrous ethanol in the column bottom, and a vapor mixture of water, ethanol, and cyclohexane/benzene. When condensed, this becomes a two-phase liquid mixture. The heavier phase, poor in the entrainer (benzene or cyclohexane), is stripped of the entrainer and recycled to the feed, while the lighter phase together with condensate from the stripping is recycled to the second column. Another early method, called extractive distillation, consists of adding a ternary component which will increase ethanol's relative volatility. When the ternary mixture is distilled, it will produce anhydrous ethanol on the top stream of the column.

With increasing attention being paid to saving energy, many methods have been proposed that avoid distillation altogether for dehydration. Of these methods, a third method has emerged and has been adopted by the majority of modern ethanol plants. This new process uses molecular sieves to remove water from fuel ethanol. In this process, ethanol vapor under pressure passes through a bed of molecular
sieve beads. The bead’s pores are sized to allow absorption of water while excluding ethanol. After a period of time, the bed is regenerated under vacuum or in the flow of inert atmosphere (e.g. N\textsubscript{2}) to remove the absorbed water. Two beds are often used so that one is available to absorb water while the other is being regenerated. This dehydration technology can account for energy saving of 3,000 btus/gallon (840 kJ/L) compared to earlier azeotropic distillation.

**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.

**Transesterification**

Animal and plant fats and oils are composed of triglycerides, which are esters containing three free fatty acids and the trihydric alcohol, glycerol. In the transesterification process, the alcohol is deprotonated with a base to make it a stronger nucleophile. Commonly, ethanol or methanol are used. As can be seen, the reaction has no other inputs than the triglyceride and the alcohol. Under normal conditions, this reaction will proceed either exceedingly slowly or not at all, so heat, as well as catalysts (acid and/or base) are used to speed the reaction. It is important to note that the acid or base are not consumed by the transesterification reaction, thus they are not reactants, but catalysts. Common catalysts for transesterification include sodium hydroxide, potassium hydroxide, and sodium methoxide.

Almost all biodiesel is produced from virgin vegetable oils using the base-catalyzed technique as it is the most economical process for treating virgin vegetable oils, requiring only low temperatures and pressures and producing over 98% conversion yield (provided the starting oil is low in moisture and free fatty acids). However, biodiesel produced from other sources or by other methods may require acid catalysis, which is much slower.

**Production methods**

**Supercritical process**

An alternative, catalyst-free method for transesterification uses supercritical methanol at high temperatures and pressures in a continuous process. In the supercritical state, the oil and methanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock, free fatty acids are converted to methyl esters instead of soap, so a wide variety of feedstocks can be used. Also the catalyst removal step is eliminated. High temperatures and pressures are required, but energy costs of production are similar or less than catalytic production routes.
Ultra- and high-shear in-line and batch reactors

Ultra- and High Shear in-line or batch reactors allow production of biodiesel continuously, semi-continuously, and in batch-mode. This drastically reduces production time and increases production volume.

The reaction takes place in the high-energetic shear zone of the Ultra- and High Shear mixer by reducing the droplet size of the immiscible liquids such as oil or fats and methanol. Therefore, the smaller the droplet size the larger the surface area the faster the catalyst can react.

Ultrasonic reactor method

In the ultrasonic reactor method, the ultrasonic waves cause the reaction mixture to produce and collapse bubbles constantly. This cavitation simultaneously provides the mixing and heating required to carry out the transesterification process. Thus using an ultrasonic reactor for biodiesel production drastically reduces the reaction time, reaction temperatures, and energy input. Hence the process of transesterification can run inline rather than using the time consuming batch processing. Industrial scale ultrasonic devices allow for the industrial scale processing of several thousand barrels per day.

Lipase-catalyzed method

Large amounts of research have focused recently on the use of enzymes as a catalyst for the transesterification. Researchers have found that very good yields could be obtained from crude and used oils using lipases. The use of lipases makes the reaction less sensitive to high FFA content, which is a problem with the standard biodiesel process. One problem with the lipase reaction is that methanol cannot be used because it inactivates the lipase catalyst after one batch. However, if methyl acetate is used instead of methanol, the lipase is not in-activated and can be used for several batches, making the lipase system much more cost effective.

Volatile Fatty Acids from Anaerobic Digestion of Waste Streams

Lipids have been drawing considerable attention as a substrate for biodiesel production owing to its sustainability, non-toxicity and energy efficient properties. However, due to cost reasons, attention must be focused on the non-edible sources of lipids, in particular oleaginous microorganisms. Such microbes have the ability to assimilate the carbon sources from a medium and convert the carbon into lipid storage materials. The lipids accumulated by these oleaginous cells can then be transesterified to form biodiesel.
Lecture :43 Combustion- Introduction and theoretical calculation of air.- Problems

Theoretical calculation of calorific value

1. Elements always combine in definite proportions to give. the products. For example 12 gm of carbon combines with 32 gm of oxygen to give 44 gm of CO₂.

\[
\begin{align*}
C + O_2 & \rightarrow \text{CO}_2 \\
12 & \quad 32 & \quad 44
\end{align*}
\]

Similarly, 4gm of hydrogen combines with 32gm of oxygen to give 36gm of H₂O.

\[
\begin{align*}
2 \text{H}_2(g) + \text{O}_2(g) & \rightarrow 2\text{H}_2\text{O}(g) \\
4 & \quad 32 & \quad 36
\end{align*}
\]

2. At STP (273 K, 1 atm) one mole of all gases occupy a volume of 22.4litres. Hence at S.T.P. 22.4 liters of CO₂ will have a weight of 44gm, its molecular weight.

3. Air contains 21 % of oxygen by volume and 23 % of oxygen by weight, Hence 1 m³ of oxygen will be supplied by

\[
\frac{1 \times 100}{21} = 4.76 \text{m}^3 \text{ of air}
\]

Similarly 1 kg of oxygen will be supplied by \( \frac{1 \times 100}{23} = 4.35 \) kg of air.

4. Molecular weight of air is 28.94mol⁻¹.

5. Minimum oxygen required = (Theoretical O₂ required) - (O₂ present in fuels).

6. The mass of flue gas is calculated by balancing the carbon in the fuel and the carbon in the flue gas.

7. Minimum O₂ required is calculated on the basis of complete combustion of fuel. If as a result incomplete combustion or CO is formed then O₂ is calculated for the conversion of CO to CO₂.

8. If the fuel contains both O₂ and H₂, the amount of hydrogen and oxygen may be present in the form of as H₂O, which is a non-combustible substance. The remaining available hydrogen takes part in the combustion reaction.

\[
\begin{align*}
2 \text{H}_2(g) + \text{O}(g) & \rightarrow 2\text{H}_2\text{O}
\end{align*}
\]
32 gm of oxygen combines with 4gm of hydrogen, Hence 1 part of hydrogen combines with 8 parts of oxygen.

\[
\text{Available oxygen} = \text{Mass of hydrogen} \cdot \frac{\text{Mass of Hydrogen}}{8}
\]

Hence, theoretical amount of oxygen required for complete combustion of 1 kg of fuel is given by the equation,

\[
\{32/12 \times C + 8[H - O/8] + S\} \text{ kg}
\]

\(C, H, S\) are masses of carbon, hydrogen and sulphur respectively per kg of the fuel. Since 1 kg of air-contains 23% of oxygen by weight, the amount of air required theoretically to burn 1 kg of fuel completely is given by equation.

\[
\frac{100}{23} \{32/12 \times C + 8[H - O/8] + S\} \text{ Kg}
\]

According to Dulong's formula for the theoretical calculation of calorific value is,

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

Where \(C, H, O\) and \(S\) represent the % of the corresponding elements in the fuel. It is based on the assumption that the calorific value \(orc, H, S\) are found to be 8080, 34500 and 2240 kcal, when 1 kg of the fuel is burnt completely.

However, all the oxygen in the fuel is assumed to be present in combination with hydrogen in the ratio \(H:O\) as 1:8 by weight. So the surplus hydrogen available for combustion is \(H - O/8\).

\[
\frac{1}{8}
\]

\[
\text{NCV (or) LCV} = [\text{HCV} - 9/100H \times 587] \text{ kcal.kg}
\]

**Theoretical calculation of minimum air requirement for combustion of a fuel**

Combustion is the process of burning any combustible substance in the presence of oxygen, which liberates energy in the form of heat and light. For efficient combustion, it is essential that the fuel must be brought into intimate contact with sufficient quantity of air or oxygen.

The combustible substance usually present in fuels, which enter into the combustion, are mainly \(C, H, S\) and \(O\). But \(N, CO_2\) and ash are incombustible matters present in the fuel, do not take any oxygen during combustion.

For the complete combustion of a given quantity of fuel can be calculated by considering the following point. Substances always combine in definite proportions, which are determined by the molecular weights of the substances.
i) Combustion of carbon

\[ C + O_2 \rightarrow CO_2 \]

12 parts by weight of carbon requires 32 parts by weight of oxygen for complete combustion. 'C' parts by weight of carbon requires \( \frac{32}{12} = 2.67 \) C

\[ (H-0/8) \text{ parts by weight of hydrogen requires } = \frac{(H-0/8) \times 32}{4} \]

\[ = 8 \text{ (H-0/8)} \]

ii) Combustion of hydrogen

When oxygen is present in the fuel, it always combines with hydrogen. The combined hydrogen does not take part in combustion reaction. Therefore, the quantity of combined hydrogen must be deduced from the total hydrogen in the fuel.

\[ 2H_2 + O_2 \rightarrow 2H_2O \]

4 parts by weight of \( H_2 \) requires 32 parts by weight \( O_2 \) (or) 2 parts by volume of \( H_2 \) require 1 part by volume of \( O_2 \)

Therefore 'H' parts by weight of hydrogen require \( \frac{32xH}{4} \) parts by weight of \( O_2 \).

iii) Combustion of carbon monoxide

\[ CO + \frac{1}{2} O \rightarrow CO_2 \]

28 \hspace{1cm} 16 \hspace{1cm} \text{(by weight)}

1 \hspace{1cm} 0.5 \hspace{1cm} \text{(by volume)}

1 volume of \( CO \) requires 0.5 volume of oxygen.

iv) Combustion of sulphur

\[ S + O_2 \rightarrow SO_2 \]
1 volume of 'S' requires 1 volume of oxygen.

v) Combustion of methane

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

Problems For the calculation of Calorific value

Calculate the gross and net calorific values of a coal sample having the following composition: C = 80%; H = 7%; O = 3%; S = 3.5%; N = 2.5% and ash 4.4%

Solution

(I) \[ \text{G.C.V} = \frac{1}{100}[8080\times\%C + 34500(\%H - \%O/8) + 2240\times\%S] \text{ kcal/kg} \]

\[ = \frac{1}{100}[8080\times 80 + 34500(7 - 3/8) + 2240\times 3.5] \text{ kcal/kg} \]

\[ = 8828.0 \text{ kcal/kg} \]

(II) \[ \text{N.C.V} = \text{G.C.V} - [0.09\times H\times 587] \text{ kcal/kg} \]

\[ = 8828 - [0.09\times 7\times 587] \text{ kcal/kg} \]

\[ = 8458.2 \text{ kcal/kg} \]

Problems based on Calculation of minimum air requirements

Calculate the Minimum volume of air required for the complete combustion of 1 m\(^3\) of a gaseous fuel containing the following composition by volume:

CO: 23%; H\(_2\): 12%; CH\(_4\): 3%; CO\(_2\): 5%; N\(_2\): 55% and O\(_2\): 2%
SOLUTION

1 m$^3$ of fuel contains

\[
\begin{align*}
23/100 &= 0.23 \text{ m}^3 \text{ of CO} \\
12/100 &= 0.12 \text{ m}^3 \text{ of H}_2 \\
3/100 &= 0.03 \text{ m}^3 \text{ of CH}_4 \\
5/100 &= 0.05 \text{ m}^3 \text{ CO}_2 \\
55/100 &= 0.55 \text{ m}^3 \text{ N}_2 \\
2/100 &= 0.02 \text{ m}^3 \text{ O}_2
\end{align*}
\]

Nitrogen and carbon dioxide are non-combustible constituents they do not burn and do not require any oxygen

The combustion equation of the remaining constituents is as follows

\[
\begin{align*}
\text{CO} + \frac{1}{2} \text{O}_2 &\rightarrow \text{CO}_2 \\
\text{H}_2 + \frac{1}{2} \text{O}_2 &\rightarrow \text{H}_2\text{O} \\
\text{CH}_4 + 2\text{O}_2 &\rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

1 m$^3$ of CO Requires = 0.5 m$^3$ of O$_2$

0.23 m$^3$ of CO Requires = 0.5*0.23/1 = 0.115 m$^3$ of O$_2$

1 m$^3$ of H$_2$ Requires = 0.5 m$^3$ of O$_2$

0.12 m$^3$ of H$_2$ requires = 0.15*0.12/1 = 0.06 m$^3$ of O$_2$

1 m$^3$ CH$_4$ of requires = 2 m$^3$ of O$_2$
0.03 m$^3$ of CH$_4$ requires = 2*0.03/1 = 0.06 m$^3$ of O$_2$

The total volume of O$_2$ required = 0.11+0.06+0.06

= 0.235 m$^3$ of O$_2$

The Net volume of O$_2$ required = Total volume of O$_2$ required - O$_2$ already present in the fuel

= 0.235 – 0.02 = 0.215 m$^3$ of O$_2$

We know that

21 m$^3$ of O$_2$ is supplied by 100 m$^3$ of air

0.215 m$^3$ of O$_2$ is supplied by = 100*0.215/21 = 1.02 m$^3$ of air

The volume of air required for the complete combustion of 1 m$^3$ of The Gaseous fuel = 1.02 m$^3$ of air
Flue Gas Analysis (Orsat's method)

The mixture of gases such as CO₂, O₂, CO, etc., coming out from the combustion chamber is called flue gases. The analysis of a flue gas would give idea about the complete or incomplete combustion process. If the flue gases contain considerable amount of CO, it indicates that incomplete combustion and it contain a considerable amount of oxygen indicates, complete combustion. The analysis of flue gas is carried out by using Orsat's apparatus.

Description of Orsat's Apparatus

It consists of a horizontal tube, having 3 way stopcock. At one end of this tube, U-tube containing fused CaCl₂ is connected. The other end of this tube is connected with a graduated burette. The burette is surrounded by a water-jacket to keep the temperature of 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 burette can be raised or lowered by raising or lowering the reservoir. The horizontal tube is also connected with three different absorption bulbs I, II and III for absorbing CO₂, O₂, CO.

**Bulb- I**: It contains 'potassium hydroxide' solution, and it absorbs only CO₂

**Bulb - II**: It contains 'alkaline pyrogallol' solution, and it absorbs only CO₂ and O₂

**Bulb:III**: It contains 'ammoniacal cuprous chloride' solution, and it absorbs only CO₂, O₂ and CO.
Orsat’s Apparatus

Working

The 3-way stopcock is opened to the atmosphere and the reservoir is raised, till the burette is completely filled with water and air is excluded from the burette. The 3-way stopcock is now connected to the flue gas supply, the flue gas is sucked into the burette, and the volume of flue gas is adjusted to 100 cc by raising and lowering the reservoir. Then the 3-way stop cock is closed.

a) Absorption of CO₂

The stopper of the bulb-1 containing KOH solution is opened and all the gas is passed into the bulb-1 by raising the level of water in the burette. The gas enters into the bulb-I, where 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 decrease in volume of the flue gas in the burette indicates the volume of CO₂ in 100 cc of the flue gas.

b) Absorption of O₂

Stopcock of bulb-I is closed and stopcock of bulb-II is opened. The gas is again sent into the absorption bulb-II, where O₂ present in the flue gas is absorbed by alkaline pyrogallol (925 g of pyrogallol + 200g of KOH in 500 ml distilled water). The decrease in volume of the flue gas in the burette indicates the volume of O₂.

c) Absorption of CO

Now stopcock of bulb-II is closed and stopcock of bulb-III is opened. The remaining gas is sent into the absorption bulb-III, where CO present in the flue gas is absorbed by ammoniacal cuprous chloride (100 g CuCl₂ + 125 mL liquor ammonia + 375 mL distilled water). The decrease in volume of the flue gas in the burette indicates the volume of CO. The remaining gas in the burette after the absorption of CO₂, O₂ and CO is taken as nitrogen.