

Q.1 Derive complete formula for determining calorific value of a solid fuel by Bomb calorimeter.

Ans. To start with 1 gm of fuel sample as a briquette is placed into the crucible and a fuse wire is connected with electrode. To absorb the combustion products of sulphur and nitrogen, 2 ml of water is poured

in the bomb. Bomb is then supplied with pure oxygen through the valve to an amount of 25 atm. The box then

placed in weighed quantity of water, in the calorimeter. The stirring is started after making necessary electrical connections, and when calorimeter indicates a steady state temperature, fuel is fined and temperature readings are

taken; the pressure is slowly released through the exhaust valve and the contents of bomb are carefully weighed for

further analysis. The heat released by combustion of fuel is absorbed by water surrounding the bomb and calorimeter.

From the above data, the calorific value can be found in the following way:

Mass of fuel taken into calorimeter = m g

mass of water taken into calorimeter =  $w$  g

water equivalent of calorimeter bomb,  
thermometer, stirrer etc. =  $w$  g

initial temp. of water in calorimeter =  $t_1$

final temp. of water in calorimeter =  $t_2$

Higher calorific value = HCV

Heat liberated by burning of fuel =  $m \times HCV$

Heat gained =  $w + w(t_2 - t_1)$

According

Heat

m

HCV

let

then

LCV

Q.2 Describe Fischer-Tropsch method of preparing synthetic petrol

Ans. The Fischer-Tropsch (FT) process, originally developed by Franz Fischer and Hans Tropsch in early 1920s, is a series of chemical reactions that involve the conversion of hydrogen and carbon monoxide into liquid hydrocarbons by using a catalyst.

This process is a key component of gas-to-liquid technology. It produces synthetic lubrication oil and synthetic fuel including natural gas, biomass or coal. Generally, these products are of higher quality than those derived through conventional means, having no sulphur or aromatics.

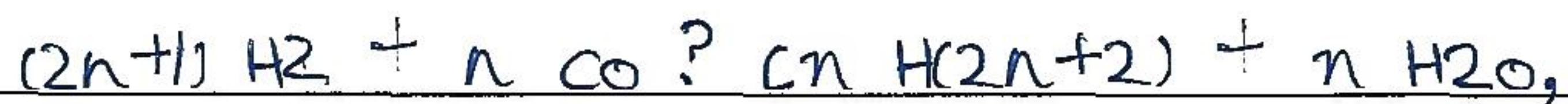
In the FT process, typical cobalt catalysts are produced using Oxford catalysts' patented technolo-

with superior stability, selectivity and activity to conventional catalysts, and without any loss of performance.

The FT process has gained importance as a source of low-sulfur diesel fuel and in addressing the cost and supply of petroleum-derived hydrocarbons.

### Process chemistry

The FT process involves a catalytic chemical reaction in which carbon monoxide ( $\text{CO}$ ) and hydrogen ( $\text{H}_2$ ) present in the synthetic gas are converted into hydrocarbons of different molecular weights based on the following equation:



where "n" is an integer.

For  $n=1$ , the reaction represents production of methanol which is considered as an undesirable by-product in most gas-to-liquids and/or coal-to-liquid applications.

The FT process conditions are chosen such that the formation of hydrocarbon liquid fuels having higher molecular weight is maximized. The process also involves some other side reactions of which the water-gas-shift reaction is predominant.



Hydrocarbons ranging from methane to higher molecular olefins and paraffin can be obtained based on the temperature, process employed and catalyst.

The FT process also yields small quantities of low molecular weight oxygenates such as organic acids and alcohol. The FT synthesis reaction is a condensation polymerization reaction of CO.

### Fischer-Tropsch catalysts

Although several catalysts can be used for Fischer-Tropsch synthesis, the transition metals of ruthenium, nickel, cobalt and iron are some of the most common catalysts. Selection of FT process catalysts is based on the diesel fuels production and high molecular weight linear alkanes.

Nickel can be also be used as the catalyst, but it tends to promote methane formation. Cobalt is more active and usually preferred over ruthenium owing to the high cost of ruthenium.

On the other hand, iron is relatively inexpensive and has high water-gas-shift activity, so it is more suitable for obtaining synthetic gas with low hydrogen:carbon monoxide ratio like those derived

through coal gasification.

In addition to the active metal, the catalysts include various promoters such as copper, potassium and high surface area binders such as alumina or silica. The presence of sulfur compounds in the synthetic gas can poison the FT catalysts.

The cobalt-based catalysts have higher sensitivity to sulfur than its iron counterparts, which in turn contributes to higher catalyst replacement costs for cobalt.

Therefore, cobalt catalysts are preferred for FT synthesis of synthetic gas derived from natural gas where the synthetic gas has relatively low sulphur content and high hydrogen to carbon monoxide ratio. Iron catalysts are preferred deriving synthetic gas from low quality feedstocks such as coal.

### Fischer-Tropsch Reactions

The reactions involved in the FT process are highly exothermic therefore, the elimination of heat is important when designing a commercial reactor. Three types of reactors are generally used for FT synthesis:

- (a) Slurry bed reactor
- (b) Fluidized bed reactor

### (c) Fixed bed reactor

Commercially, all three types of reactors are in use. Heavy FT liquid hydrocarbons are produced in Ange reactors, the multitubular fixed-bed reactors developed by Ruhrochemie and Lurgi and used by Sasol.

Most of these Ange reactors are now replaced by slurry-bed reactors, which are regarded as the state-of-the-art technology for low temperature FT synthesis. Slurry-bed FT reactors have higher conversion rates and better temperature control.

Fluidized-bed FT reactors were developed for producing low molecular gaseous hydrocarbons and gasoline through high temperature FT synthesis.

They were originally developed in a circulating mode and have been replaced by Advanced Synthal reactors with fixed fluidized bed type design. These reactors have high throughputs.

Q.3 List out the steps involved in proximate analysis of coal sample. What information can be extracted from this data?

Ans. Proximate analysis-

Proximate analysis of coal was developed as a simple method for characterizing and determining the distribution of various constituents.

found in coal. Here the coal sample is subjected to heat under specified conditions, and the generated products can be grouped into:  
i) moisture; ii) volatile matter iii) fixed carbon, iv) ash, the inorganic residue remaining after combustion. i.e. for the determination of volatile matter, moisture, ash and fixed carbon

#### Determination of Moisture content (M)

As all coals are mined wet they are always associated with some amount of moisture. The moisture can be physically or chemically bound, due to its nature, origin and occurrence.

Extraneous and inherent moisture must be properly differentiated. Extraneous moisture evaporates just by exposing coal to sunlight, even the coal still have moisture inside it or it should be removed while keeping the sample in a furnace for 2 hours at 35 to 40°C. This internal moisture can be removed by heating coal at 100°C. The mode of occurrence and handling of coal is responsible for the quantity of external but the air-dried moisture is associated due to the inherent hygroscopic nature of the coal.

#### Procedure

- About 1g of air-dried coal sample finely powdered

c-2/2

crucible.

- (a) It is then placed inside an electric hot air oven (plate 4.1) which was maintained at 1080°C and allowed to remain there 1.5 hours
- (b) It was then taken out with a pair of tongues, cooled in desiccators for about 15 minutes and then weighed.
- (c) The loss in weight was reported as moisture (on percentage basis).

Moisture is calculated as per the following formula.

$$\text{Moisture \%} = (Y - Z / Y - X) \times 100$$

where,

X = weight of empty crucible, g

Y = weight of crucible and coal sample before heating

Z = weight of crucible and coal sample after heating

### Determination of Ash content (A)

The residue left after the combustion of coal under some specified conditions is called the coal ash. It is formed as the result of chemical changes that take place in the mineral matter and does not occur as such in coal. Hence ash and mineral matter of coal are not identical.

Two types of ash forming materials in coal are mainly the extraneous and inherent mineral matters.

The extraneous mineral matter comprises of material

like calcium, magnesium and ferrous carbonates, pyrite, magnetite, clays, shales, sand and gypsum. The extraneous mineral matter builds on its origin by two types that are given below:

- (a) The substances which got coupled with the rotting vegetable material during its alteration to coal, which is difficult to remove by mechanical methods,
- (b) Rocks and dirt that mixed up during mining and handling of coal.

The intrinsic mineral matter is the inorganic elements linked with organic components of coal. The origin of such materials is most probably from the plant materials from which the coal is produced. When the total quantity of ash is pertained ash from intrinsic mineral matter becomes insignificant as far as the total quantity of ash is concerned. Indian coals suffer from the major shortcoming, that the mineral matter contained is not only high, but of intimately linked type, due to its drift origin. Ash is quantitatively and qualitatively different from the mineral matter originally present in coal because the numerous modifications that occur, such as loss of water from silicate minerals, loss of carbon dioxide from carbonate minerals, oxidation of iron pyrite to iron oxide, and fixation oxides of sulphur by bases such as

calcium and magnesium. In fact, combustion circumstances determine the amount to which the weight change takes place and it is necessary that standardized operations should be closely followed to ensure productivity.

#### Procedure:

The empty crucible was cleaned by heating in a muffle furnace for one hour at 800°C so that other mineral matter if presents get burnt. It was taken out, cooled to room temperature and the weight is taken. Approximately 1 gm of coal sample was weighed in the crucible and placed in a muffle furnace at 450°C for 30 minutes & the temperature of the furnace was raised to 850°C for 1 hour. The crucible was taken out and placed in desiccators and weighed.

Ash is calculated as per the following formula:

$$\text{Ash} \% = (z - x) / (y - x) \times 100$$

where,

$x$  = weight of empty crucible in grams

$y$  = weight of coal sample and crucible in grams  
(Before heating)

$z$  = weight of coal sample and crucible in grams (After heating)

#### Determination of volatile Matter (VM)

When a coal sample is heated in specified equipment

under prescribed conditions in Indian standard, the loss of mass in coal, corrected for moisture, is referred to as volatile matter of coal. Some of the components of coal transformed volatile matter are hydrogen, carbon monoxide, methane and other hydrocarbons, vapors, ammonia, some organic sulphur and oxygen containing depens and some incombustible such as CO and water vapor, all of which come from the disintegration of organic matter in coal. Inorganic materials in coal are responsible for the presence of the water of hydration of mineral matter, carbon dioxide from carbonates and hydrogen chloride from inorganic chlorides to the volatile matter.

#### Procedure

For the determination of volatile matter a special volatile matter silica crucible (38 mm height, 25 mm external diameter and 22 mm internal diameter) was used. The empty volatile

matter crucible was weighed. 1g of coal sample (-2/2 size) was weighed in the volatile matter crucible and it was placed inside a muffle furnace maintained at 925°C with the lid covering the crucible for 7 minutes. The heating was carried out exactly for seven minutes, after which the

was removed, cooled in air, then in desiccators and weighed again. The calculation was done as per the following formula:

$$\% \text{ volatile Matter} = (Y - Z) / (Y - X) \times 100 - \text{Moisture \%}$$

where,

$X$  = weight of empty crucible, g

$Y$  = weight of crucible and coal sample before heating g

$Z$  = weight of crucible and coal sample after heating , g

### Determination of Fixed carbon (FC)

After the determination of moisture, volatile matter and ash the mathematical remaining is fixed carbon by definition. Fixed carbon plus ash present the approximate yield of coke from coal. The value of fixed carbon is evaluated by subtracting the resultant summation of moisture (M), volatile matter (VM) and ash (A) from 100 with all parts on the same moisture reference basis

$$FC = 100 - (M + VM + A)$$

Q.4 Define calorific value. What are the different units and types of calorific value?

Ans. Calorific value Definition

"calorific value refers to the amount of heat produced by unit volume of a substance by complete combustion"

what is the calorific value?

calorific value is the amount of heat energy present in food or fuel and which is determined by the complete combustion of specified quantity at constant pressure and in normal conditions. It is also called calorific power. The unit of calorific value is kilojoule per kilogram i.e. kJ/kg.

water vapour is generated in the combustion process the heat should be recovered by using certain techniques. If the heat contained in the water could be recovered then it has high calorific value. heat contained in the water vapor could not be recovered when it has low calorific value.

The efficiency of fuel or food mainly depends on the calorific value. If the value is high, its efficiency will also be high. If the value is low, its efficiency would also decrease. calorific value is directly proportional to its efficiency.

### calorific value of Fuel

Here is the detailed list of fuels and their calorific values:

#### Fuel      calorific value of Fuel

Cow Dung      8000

wood      22000

coal	33000
Biogas	40000
Diesel	45000
Kerosene	45000
Petrol	45000
Methane	50000
LPG	55000

Importance of calorific value-

It is very important to have a knowledge of the calorific value of fuel to carry out our day-to-day activities. This knowledge helps us to determine the amount of energy we transport. The gas shippers & suppliers require this information to bill gas consumers. It also helps to determine transportation charges of gas shippers and suppliers.

Q.5 The higher calorific value of a bituminous coal is given 36,000 kJ/kg. In an experiment 0.83 g of this coal is burnt under 1.2 kg of water in a calorimeter. Due to combustion, the temperature of water rises by 3.9 °C. calculate the water equivalent of the calorimeter.

Specific heat of water = 4.2 kJ/kg

Ans. Calorific value of a bituminous coal = 36,000 kJ/kg.

Mass of coal taken =  $0.83\text{g} = 0.83/1000 \text{kg}$

Rise in temp. = 3.9°C

Gross value = (wtw2)  $\times$  Sp. Heat  $\times$  Rise in temp

Mass of coal

$$3600 = [1.2 = w_2 \times 4.2 \times 3.9] / (0.83/1000)$$

$$w_2 = 0.409 \text{ Kg}$$

Q.6 A sample of fuel having following percentage composition: C=72%, H=5%, O=4%, N=2%, S=3%, ash= 8% and moisture= 6% calculate the quantity of air required for the complete combustion of 1 kg fuel.

Ans. Given that 1 Kg of fuel contains-

$$C = 720 \text{ gm}$$

$$H = 50 \text{ gm}$$

$$S = 30 \text{ gm}$$

$$O = 42 \text{ gm}$$

$$\text{Net O}_2 = [(3 \times 3)/12 \times 720 + (16/2) \times 50 + (32/32) - 40] = 2310 \text{ gm}$$

$$\text{So quantity of air required} = \text{Net O}_2 \times 100/23$$

$$= 10043.5 \text{ gm}$$

$$= 10.043 \text{ kg} -$$