

FUELS

Syllabus: Coal – Proximate and ultimate analysis – Numerical problems based on analysis – Calorific value – HCV and LCV – Problems based on calorific values- Petroleum – Refining – Cracking – Petrol – Diesel- knocking; Gaseous fuels – Natural gas – LPG, CNG – Combustion – Problems on air requirements.

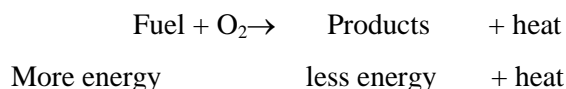
Objectives: A broad understanding of the more important fuels employed on a large scale is necessary for all engineers to understand energy – related problems and solve them.

- ❖ *Introduction*
- ❖ *Classification of fuels*
- ❖ *Characteristics of a good fuel*
- ❖ *Calorific value – Bomb calorimeter- related problems*
- ❖ *Analysis of Coal – Proximate and Ultimate analysis- related problems*
- ❖ *Theories of origin of petroleum*
- ❖ *Refining of petroleum*
- ❖ *Cracking*
- ❖ *Synthetic petrol*
- ❖ *Refining of gasoline*
- ❖ *Gaseous fuels*
- ❖ *Combustion processes*
- ❖ *Problems relating to combustion*

1. INTRUCTION: “Fuel is a substance, containing carbon as a main constituent, which on burning gives large amount of heat, which can be used economically for domestic and industrial purposes”.

Ex: Wood, coal, kerosene, petrol, diesel, natural gas, producer gas, oil gas etc.

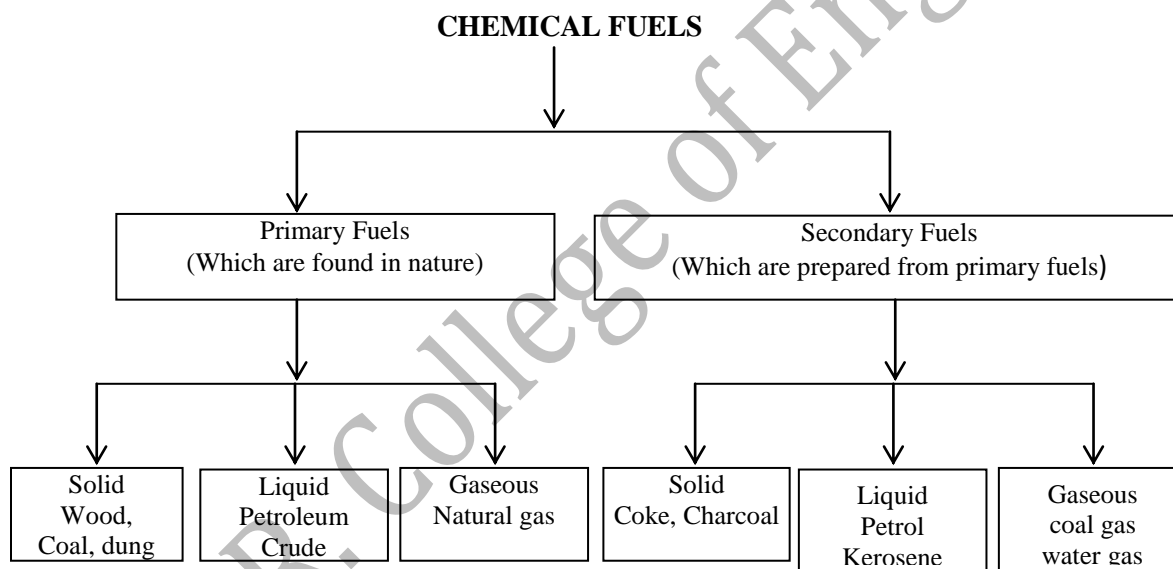
During the combustion process the reactants produce products like CO_2 , H_2O etc. of lower energy. The energy released during the combustion process is the difference in the energy of the reactants and the products.



2. Classification of fuels

Fuels are classified according to their occurrence as well as their physical state.

1) Natural or primary fuels 2) Artificial or secondary fuels



Fuels that are found and obtained from nature are natural fuels. E.g: Coal, petroleum etc.

Fuels that are prepared artificially from primary fuels are secondary or artificial fuels.

Eg: Kerosene, producer gas etc.

On the basis of physical state, fuels are classified as solid, liquid and gaseous fuels.

3. Characteristics of a good fuel

1. A fuel should possess high calorific value, resulting in large amount of heat per unit mass.
2. It should possess moderate ignition temperature.
3. It should have low moisture content, since high value reduces its heating value.

4. A good fuel should have low content of non-combustible matter and ash.
5. Moderate velocity of combustion is required to prevent loss of heat by radiation.
6. Fuel on burning should not give toxic or poisonous gases like CO, H₂S, and SO₂ etc.
7. A good fuel should be readily available in bulk at a low cost.
8. The fuel must be easily transported and stored safely.
9. The combustion of a fuel should be easily controllable. The fuel should not undergo spontaneous combustion without smoke.

Comparison between Solid, Liquid and fuel gases

	Solid fuel	Liquid fuel	Gaseous fuel
1	Combustion is slow	Quick combustion	Combustion takes place rapidly
2	Transport is sometimes difficult.	It can easily be transported through pipes.	It can easily be transported through pipes and containers.
3	Storage is safe	There is greater risk in storage.	There is the greatest risk in storing.
4	Calorific value is less.	Calorific value is higher.	Calorific value is highest.
5	Ash and smoke are produced and their disposal is a problem.	There is no ash problem but it may produce smoke.	Neither ash nor smoke are produced.
6	They cannot be used in internal combustion engines.	They can be used in internal combustion engines	They can also be used as internal combustion engines.

4. Calorific value

The heat liberated by fuels on combustion is not same for all fuels. Hence, the efficiency of a fuel is measured by its calorific value. Calorific value is defined as **“the total quantity of heat liberated, when a unit mass (or) volume of the fuel is burnt completely in air or oxygen”**.

Units of calorific value:

The unit of calorific value for solid or liquid fuels is cal/g or K.cal/g or B.Th.U/lb. For gaseous fuels it is K.Cal/ m³ or B.Th.U/ft³.

1. **Calorie:** It is the amount of heat required to raise the temperature of one gram of water through one degree centigrade.
2. **Kilo calorie:** The quantity of heat required to raise the temperature of 1000g or one kilogram of water through one degree centigrade. This is the unit in metric system.

$$1 \text{ Kcal} = 1000 \text{ cal}$$

3. **British Thermal Unit (B.Th.U.)** : The amount of heat required to raise the temperature of one pound of water (454g) by one degree fahrenheit. This is the unit in British system.

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

4. **Centigrade Heat Unit (C.H.U.)**: It is the amount of heat required to raise the temperature of one pound of water by one degree centigrade.

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

4.1. Higher (or) Gross Calorific Value (HCV or GCV)

It is “the total amount of heat produced, when unit mass or volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature”. This value is determined by bomb calorimeter.

4.1.2. Lower (or) Net Calorific Value (LCV or NCV)

This is “the net heat produced, when a unit mass or volume of the fuel has been burnt completely” and the products are allowed to escape.

4.2. Bomb calorimeter – Experimental determination of calorific value of a fuel

It is the apparatus used for the determination of calorific values of solid and liquid fuels.

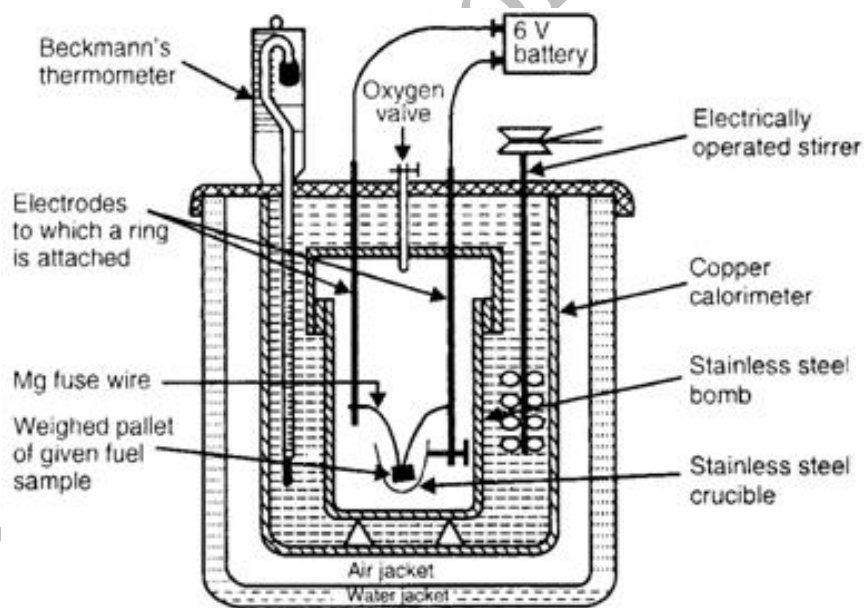


Fig. 1. Bomb calorimeter.

A known mass of the fuel is burnt in an excess supply of oxygen and the quantity of heat is absorbed by previously weighed water in a copper calorimeter and is measured by method of mixtures. The apparatus consists of a strong cylindrical stainless steel bomb inside which the fuel sample is placed. The bomb is an air tight vessel with a heating element connected to a 6V battery. The bomb lid has an oxygen

inlet valve which extends out of the bomb as outlet. Inside the bomb one of the electrodes has a small ring attachment to hold a crucible. The sample whose calorific value is to be measured is placed in the crucible along with a piece of magnesium wire. The terminals of magnesium fuse wire are connected *via* the two electrodes to the battery.

The bomb is placed in a copper calorimeter filled with water of known weight. This is protected by an air jacket and a water jacket to prevent any loss of heat by radiation etc.. The copper calorimeter whose water equivalent is known, is provided with a Beckmann thermometer and a stirrer. The stirrer can be electrically operated. The Beckmann's thermometer can read the temperature difference accurately.

Experiment: A known mass of the given fuel is taken in to the crucible. The fine magnesium wire touching the fuel sample is stretched across the electrodes. The bomb lid is tightly screwed and bomb is filled with oxygen at 25 atmosphere pressure. The bomb is then lowered into the copper calorimeter, containing a known mass of water. The stirrer is operated and the initial temperature of the water is noted. The sample is burnt operating the and heat is liberated. Now the maximum temperature attained after stirring the contents steadily is recorded.

Calculations:

x = Mass of fuel sample taken in crucible.

w = mass of water in the calorimeter.

W = Water equivalent in grams of calorimeter, stirrer, thermometer, bomb etc.

t_1 = Initial temperature of water in calorimeter.

t_2 = Final temperature of water in calorimeter.

L = Higher calorific value (HCV) in fuel in cal/g

\therefore Heat liberated by burning of fuel = $x \cdot L$

Heat absorbed by water apparatus etc. = $(W+w) (t_2-t_1)$

By method of mixtures, heat liberated by the fuel = Heat absorbed by water & apparatus.

Thus $x \cdot L = (W+w) (t_2-t_1)$

$$\text{(HCV of fuel (L))} = \frac{(W+w)(t_2-t_1)}{x} \text{ cal/g or kcal/kg}$$

Note: The water equivalent of the calorimeter is determined by burning a fuel of known calorific value and using the above equation. The fuels used for this purpose are benzoic acid (HCV = 6,325 Kcal/kg) or naphthalene (HCV = 9,688 K.cal/kg).

If H = Percentage of hydrogen in fuel.

$$\text{Mass of H}_2\text{O from 1g of fuel} = \frac{9H}{100} = 0.09H \text{ g}$$

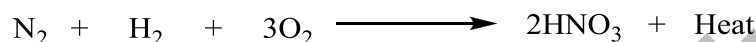
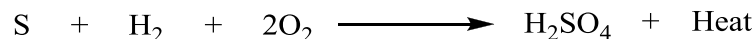
∴ Heat taken by water in forming steam

$$= 0.09H \times 587 \text{ cal} \quad [\because \text{Latent heat of steam} = 587 \text{ cal/g}]$$

∴ LCV = HCV – Heat taken by water in forming steam

Corrections: To get more accurate results, the following corrections are applied.

- i) **Fuse wire correction:** The heat liberated also includes the heat evolved by ignition of the magnesium fuse wire. This must be subtracted from the experimentally obtained result.
- ii) **Acid correction:** Fuels containing S and N are oxidized under high pressure and temperature to H_2SO_4 and HNO_3 respectively.



Formation of these acids is an exothermic reaction. So the measured heat also includes the heat given out during the acid formation. The correction for 1mg of S is 2.25 cal, for 1 ml of N/10 HNO_3 formed is 1.43 cal. The values must also be subtracted from the experimental result.

- iii) **Cooling correction:** The loss of heat due to convection, conduction and radiation along with correction due to stirring evaporation must also have to be considered. This correction is generally little and ignored. But for rigorous results, correction has to be considered. For this the time taken to cool the water in the calorimeter from maximum temperature to room temperature is noted. From the rate of cooling ($dt^\circ\text{C}/\text{minute}$) and the actual time taken for cooling (t minutes), the cooling correction of $dt \times t$ is added to the raise in temperature.

$$L = \frac{(W + w)(t_2 - t_1 + \text{cooling correction}) - (\text{acid} + \text{fuse correction})}{\text{Mass of fuel (x)}}$$

Problems :

1. 0.72 gram of a fuel containing 80% carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3°C to 29.1°C . if the calorimeter contains 250 grams of water and its water equivalent is 150 grams, calculate the HCV of the fuel. Give your answer in kJ/kg .

Solution: Here

$$x = 0.72\text{g}, W = 250\text{g}, w = 150\text{g}, t_1 = 27.3^\circ\text{C}, t_2 = 29.1^\circ\text{C}$$

$$\begin{aligned} \therefore \text{HCV of fuel (L)} &= \frac{(W+w)(t_2-t_1)}{x} \text{ kcal/kg} \\ &= \frac{(250+150) \times (29.1-27.3)}{0.72} \text{ kcal/kg} = 1000 \times 4.2 \text{ kJ/kg} = 4200 \text{ kJ/kg} \end{aligned}$$

2. On burning 0.83 g of a solid fuel in a bomb calorimeter, the temperature of 3,500 g of water increased from 26.5 °C to 29.2°C. Water equivalent of calorimeter and latent heat of steam are 385.0 g and 587.0 cal/g respectively. If the fuel contains 0.7% hydrogen, calculate its gross and net calorific value.

Solution: Here weight of fuel (x) = 0.83 g ; wt. of water (W) = 3,500 g ; water equivalent of calorimeter (w) = 385 g ; (t_2-t_1) = (29.2 °C – 26°C) = 2.7 °C ; percentage of hydrogen (H) = 0.7% ; latent heat of steam = 587 cal/g.

$$\begin{aligned} \therefore \text{GCV of fuel} &= \frac{(W+w) (t_2- t_1)}{x} \text{ cal/g} \\ &= \frac{(3500 + 385) \times 2.7}{0.83} = 12638\text{cal/g} \end{aligned}$$

$$\begin{aligned} \text{Net calorific value} &= [\text{GCV} - 0.09 H \times 587] = (12683 - 0.09 \times 0.7 \times 587) \\ &= (12,683 - 37) \text{ cal/g} = 12,601 \text{ cal/g} \end{aligned}$$

3. Wt. of coal sample (x) = 0.92 g; wt. of water (W) = 550 g; water equivalent of calorimeter (w) = 2,200 g; temperature rise (t_2-t_1) = 2.42 oC; acid correction = 50.0 cal; fuse wire correction = 10.0 cal; latent heat of steam = 587 cal/g; percentage of H = 6%.

$$\begin{aligned} \therefore \text{GCV of fuel} &= \frac{(W+w) (t_2-t_1) - [\text{Acid} + \text{fuse corecctions}]}{x} \\ &= \frac{(550 + 22,00) \times 2.42 - [50+10]}{0,92} = 7,168 \text{ cal/g} \end{aligned}$$

$$\begin{aligned} \text{Net calorific value} &= [\text{GCV} - 0.09 H \times 587] = (7,168 - 0.09 \times 6 \times 587) \\ &= 6855.3 \text{ cal/g} \end{aligned}$$

5. Analysis of coal

The composition of coal varies from place to place, hence its analysis becomes necessary for selection of proper coal and fixing the cost. To assess the quality of coal, there are two types of analyses.

1. Proximate analysis
2. Ultimate analysis

5.1. Proximate analysis: The analysis is proximal and hence the name. It is a quantitative analysis for the determination of the following parameters.

- a) **Moisture:** About 1g of finely powdered coal is air-dried and weighed in a silica crucible. The crucible is placed in an electric hot-air-oven, maintained at 105- 110 °C for an hour. The crucible is

then taken out, cooled in a desiccator and weighed for loss in weight, which is reported as moisture content on percentage basis.

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

Some percentage of moisture is required to prevent clinkering of coal which prevents free air flow in to the furnace. But, high percentage of moisture content is undesirable, since it reduces the calorific value, increases the cost of transport and considerable amount of heat is lost in evaporation.

- b) **Volatile matter:** The dried sample of coal left in the crucible in (a) is covered with a lid and placed in a muffle furnace maintained at $925^{\circ} \pm 20^{\circ}\text{C}$ for 7 minutes. The crucible is cooled in air, then in desiccator and weighed again. The loss in weight is reported as volatile matter on percentage basis.

$$\text{Percentage of volatile matter} = \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Weight of coal sample taken}} \times 100$$

If this value is high, it causes smoke, long flames and decreases the calorific value. In some cases, the smoke from volatile matter gives useful by-products.

- c) **Ash:** The residual coal in the crucible in (b) is then heated without lid in a muffle furnace at $700^{\circ} \pm 50^{\circ}\text{C}$ for half-an-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.

$$\text{The percentage of ash} = \frac{\text{Weight of ash formed}}{\text{Weight of coal taken}} \times 100$$

Lower the value of ash content gives better quality of coal. High ash content decreases the calorific value, favours clinkering and creates problems of disposal of ash.

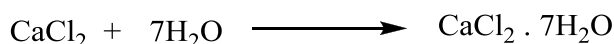
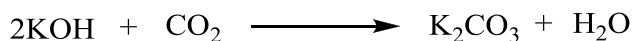
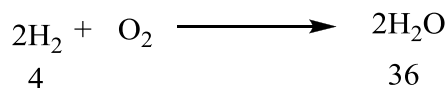
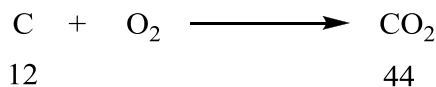
- d) **Fixed Carbon:** It represents the quantity of carbon in the coal obtained by subtraction of all the above from 100.

$$\text{Percentage of fixed carbon} = 100 - \% \text{ of } \{ \text{moisture} + \text{volatile matter} + \text{ash} \}$$

High carbon percentage gives quality coal, increase in its fuel value and is desirable property.

5.2. Ultimate Analysis: It involves elemental analysis and is qualitative. It involves the determination of C, N, S and oxygen.

- a) **Carbon and hydrogen:** About 1g of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO_2 and H_2O respectively. The gaseous products of combustion are absorbed respectively in KOH and CaCl_2 tubes of known weights. The increase in weights of tubes is determined.



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

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

Significance: Higher percentage of carbon and hydrogen gives better quality of coal and higher is the calorific value.

- b) **Nitrogen:** About 1g of finely powdered and weighed coal is heated with concentrated H_2SO_4 along with K_2SO_4 (catalyst) in a long necked flask (Kjeldahl's flask). After the solution becomes clear, it is treated with an excess of KOH solution and 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.

$$\text{Percentage of N} = \frac{\text{Volume of acid used} \times \text{normality} \times 14}{\text{Weight of coal taken} \times 1000} \times 100$$

Significance: Nitrogen does not contribute to the calorific value. Hence its presence is undesirable. Thus a good coal should have very low percentage of nitrogen.

- c) **Sulphur:** It is determined from the washings obtained from the known mass of coal, used in bomb calorimeter. During the combustion of coal, the sulphur is converted into sulphate. The washings are treated with barium chloride solution, when barium sulphate precipitate is precipitated. This precipitate is filtered, washed, heated and cooled to obtain a constant weight.

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

Significance: S contributes to the heating value of coal by combustion, but it produces acids (hydrolysis of products of combustion like SO_2 and SO_3), which have harmful effects of corroding the equipment and also cause atmospheric pollution.

- d) **Oxygen:** Percentage of oxygen = 100 – percentage of (C + H + S + N + ash)

Significance: High oxygen percentage indicates a high percentage of moisture, which decreases the calorific value.

5.3 Theoretical calculation of calorific value of a fuel

The calorific value of a fuel can be approximately computed by noting the amounts of the constituents of the fuel. The higher calorific values of some of the chief constituents of a fuel are

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

The oxygen, if present in fuel, is assumed to be present in combined form with hydrogen, i.e., in the form of fixed hydrogen [H_2O].

The amount of hydrogen available for combustion is

$$= \text{Total mass of Hydrogen in fuel} - \text{Fixed Hydrogen}$$

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

$$(\because 8 \text{ parts of oxygen combine with one part of hydrogen to form } H_2O)$$

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

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

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

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

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

Problems on HCV, LCV calculations:

Worked out example 1

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

Solution

According to Dulong's formula, Gross Calorific Value (GCV) or Higher Calorific Value (HCV) is

The percentage of O is $100 - [\text{percentage of C} + \text{H} + \text{S} + \text{N} + \text{Ash}]$

From the above data, Percentage of O is 0

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

$$\begin{aligned}
 &= \frac{1}{100} \left[8,080 \times 85 + 34,500 \left(8 - \frac{0}{8} \right) + 2,240 \times 1 \right] \text{kcal/kg} \\
 &= \frac{1}{100} [686,800 + 276,000 + 2,240] \text{kcal/kg} \\
 &= \frac{1}{100} [965,040] \text{kcal/kg} = 9,650.4 \text{ kcal/kg}
 \end{aligned}$$

$$\begin{aligned}
 \text{Net Calorific Value (NCV)} &= (\text{GCV} - 0.09\text{H} \times 587) \text{kcal/kg} \\
 &= (9,650.4 - 0.09 \times 8 \times 587) \text{kcal/kg} \\
 &= 9,227.8 \text{ kcal/kg}
 \end{aligned}$$

Worked out example 2

0.72 gram of a fuel containing 80% carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3° to 29.1°C. If the calorimeter contains 250 grams of water and its water equivalent is 150 grams, calculate HCV of the fuel. Give your answer in kJ/kg.

Solution

Here $x = 0.72\text{g}$, $W = 250\text{ g}$, $w = 150\text{ g}$, $t_1 = 27.3^\circ\text{C}$, $t_2 = 29.1^\circ\text{C}$.

$$\begin{aligned}
 \text{HCV of fuel (L)} &= \frac{(W + w)(t_2 - t_1)}{x} \text{ kcal/kg} \\
 &= \frac{(250 + 150) \times (29.1 - 27.3) \text{ kcal}}{0.72} = 1,000 \times 4.2 \text{ kJ/kg} = 4200 \text{ kJ/kg}
 \end{aligned}$$

Worked out example 3

A sample of coal contains; C = 93%; H = 6% and ash = 1%. The following data were obtained when the above coal was tested in a bomb calorimeter.

- Weight of coal burnt = 0.92 g
- Weight of water taken = 550 g
- Water equivalent of bomb and calorimeter = 2,200 g
- Rise in Temperature = 2.42 °C
- Fuse wire correction = 10.0 cal
- Acid correction = 50.0 cal

Calculate the gross and net calorific value of the coal, assuming that latent heat of condensation of steam as 580 cal/g.

Solution

Weight of coal sample (x) = 0.92g; weight of water (W) = 550g; water equivalent of calorimeter (w) = 2,200g; temperature rise ($t_2 - t_1$) = 2.42°C; acid correction = 50.0 cal; fuse wire correction = 10.0 cal; latent heat of steam = 580 cal/g; percentage of hydrogen = 6%

$$\therefore \text{GCV} = \frac{(W + w)(t_2 - t_1) - [\text{Acid} + \text{Fuse Correction}]}{x}$$

$$= \frac{(550 + 2200) \times 2.42 - [50 + 10] \text{cal}}{0.92 \text{ g}} = 7,168.5 \text{ cal/g}$$

$$\therefore \text{NCV} = [\text{GCV} - 0.09 \times \text{H} \times \text{Latent heat of steam}]$$

$$= (7,168.5 - 0.09 \times 6 \times 580) \text{ cal/g}$$

$$= 6,855.3 \text{ cal/g}$$

Problems on analysis of coal

Worked out example 1

A sample of coal was analyzed as follows: Exactly 2.500g was weighed into a silica crucible. After heating for one hour at 110°C, the residue weighed 2.415g. The crucible next was covered with a vented lid and strongly heated for exactly seven minutes at 950 ±20°C. The residue weighed 1.528g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weight 0.245g. Calculate the percentage results of the above analysis.

Solution:

$$\text{Mass of the moisture in the coal sample} = 2.500 - 2.415 = 0.085$$

$$\text{Mass of volatile matter} = 2.415 - 1.528 = 0.887\text{g}$$

$$\text{Mass of ash} = 0.245\text{g}$$

$$\text{Percent of Moisture} = \frac{0.085 \times 100}{2.500} = 3.40\%$$

$$\text{Percent of volatile matter} = \frac{0.887 \times 100}{2.500} = 35.48\%$$

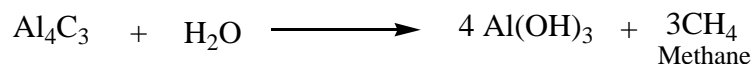
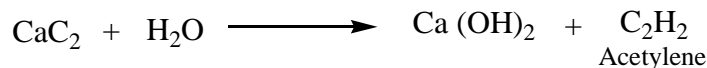
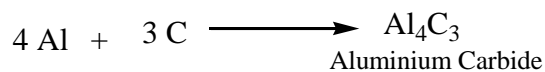
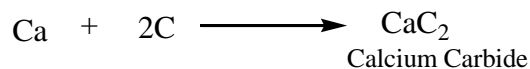
$$\text{Percent of ash} = \frac{0.245 \times 100}{2.500} = 9.80\%$$

$$\text{Percent of fixed carbon} = 100 - (3.40 + 35.48 - 9.80) = 51.32\%$$

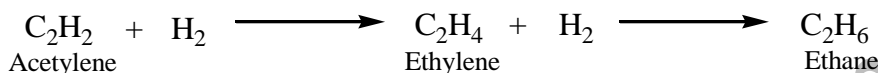
6. Origin of petroleum

Petroleum (*petra* = rock, *oleum* = oil) is a dark green fluorescent mineral oil found well deep in earth's crust mainly composed of solid, liquid and gaseous hydrocarbons. There are two main theories for the origin.

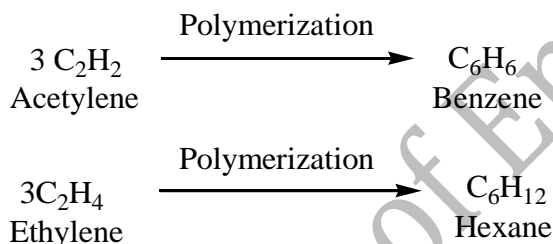
6.1. Carbide theory: This theory is known as inorganic theory of petroleum. According to this theory the carbides which are formed from a reaction between carbon and metals at high temperature and pressure, are acted upon by steam to give hydrocarbons.



The unsaturated hydrocarbons which are produced along with the saturated hydrocarbons react with hydrogen to produce saturated hydrocarbons.



The unsaturated hydrocarbons also get polymerized in the presence of metals.



This theory provides us a proof of the inorganic origin of the petroleum, but it does not provide any satisfactory explanation for the existence of sulphur and nitrogen. The presence of optically active compounds cannot be visualized on the basis of this theory.

6.2. Engler's theory: This theory explains the origin of petroleum to be of organic type. According to this theory, petroleum is generated from animal and vegetable matter (especially aquatic) under the influence of high temperature and pressure underneath the crust of earth. The organic theory has been supported by the geologists because it gives satisfactory explanation for the presence of S and N, optically active organic compounds, fossils and brine in petroleum deposits. The theory was further supported by the fact that when the destructive distillation of fish oil and other animal fats under high temperature and pressure was carried out in laboratory, a petroleum-like liquid containing N, S and optically active compounds was obtained.

However, the theory fails to account for a) the presence of chlorophyll in the petroleum b) the presence of coal deposits found near the oil fields and c) the presence of resins in the oil.

The modern theory is an admixture of the two theories proposed above. Due to the pressure and temperature so developed and radioactivity of various compounds, the bacterial decomposition resulted in the formation of petroleum. The existence of chlorophyll and resins provide a proof to this theory.

Composition of petroleum: Crude petroleum obtained from different places has a composition which varies within a narrow range. The ultimate analysis shows.

Carbon = 79.5 to 87.1%, Hydrogen = 11.5 to 14.8%

Sulphur = 0.1 to 3.5%, Nitrogen + Oxygen = 0.1 to 0.5%

Metals have been found in the petroleum ash. The most widely occurring metals include silicon, iron, aluminium, calcium, magnesium, nickel and sodium.

Mining of petroleum: This is done by drilling holes in the earth's crust and sinking pipes up to the oil bearing porous rocks. Oil usually gushes out itself due to hydrostatic pressure of natural gas. Alternatively, it may be mechanically pumped by using either lift pump or air-lift pump. The latter consists of two co-axial pipes, lowered into the base of oil bed, compressed air being forced through the outer pipe, where by crude petroleum comes out through the inner pipe. The crude oil is conveyed to refinery by pipelines.

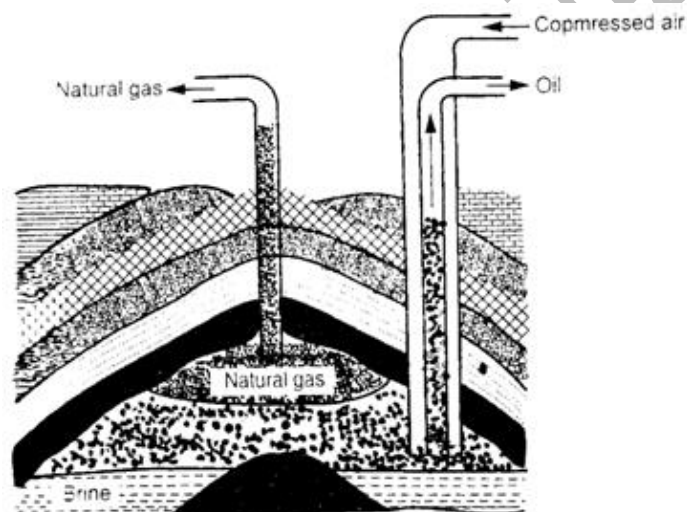


Fig. 2. Mining of crude oil and use of air-lift pump.

7. Refining of petroleum

The crude oil obtained from the mine is not fit to be marketed. So the crude oil is isolated into various fractions by fractional distillation and finally converted into the desired products. This process is known as “refining of crude oil”. The crude is a mixture of solid, liquid and gaseous impurities. It is allowed to stand undisturbed for some time, when heavy solids settle and gases evaporate. The supernatant liquid is centrifuged, when solids are removed. The further process involves the following stages.

1. Separation of water (Cottrell's Process)
2. Removal of harmful sulphur compounds
3. Fractional distillation

7.1. Removal of water (Cottrell's apparatus): The crude from the oil well is an extremely stable emulsion of oil and salt water. The process of removal of oil from water consists in allowing the crude to flow between two highly charged electrodes to destroy the emulsion. The colloidal water – droplets coalesce to form large drop which separates out from the oil.

7.2. Removal of harmful sulphur compounds: This involves the treatment of crude oil with copper oxide. The sulphur compounds form insoluble copper sulphide removed by filtration.

7.3. Fractional distillation: The crude oil is heated to about 400°C in an iron retort, where all the volatile constituents evaporate except the residue asphalt or coke. The hot vapors are then passed into a fractionating column, which is a tall cylindrical tower containing a number of horizontal steel trays at short distances. Each tray is provided with a small chimney covered with a loose bubble cap. As the vapors go up through the bubble cap, they become gradually cooler and fractional condensation takes place at different heights of the column. Fractions having higher boiling points condense first; while the lower boiling fractions follow gradually in the stages of the fractionating column.

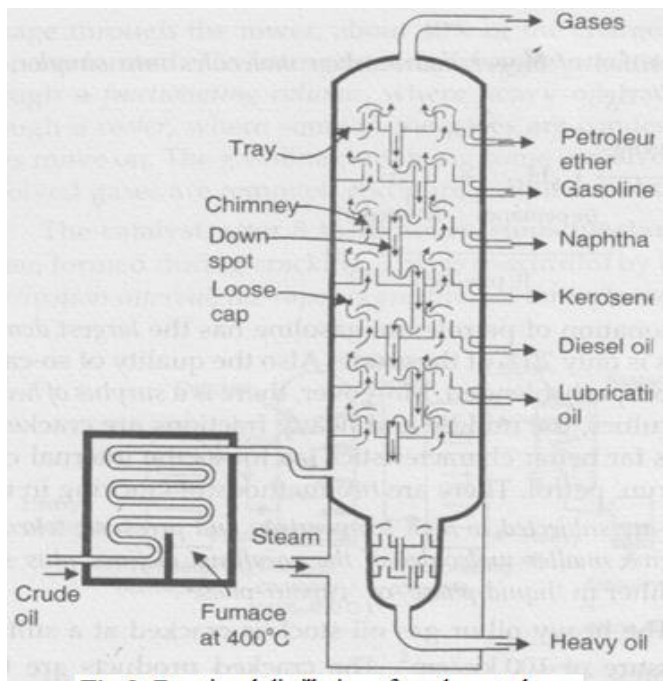


Fig.3. Fractional distillation of crude petroleum.

The following are the various fractions obtained by the fractionation of crude oil:

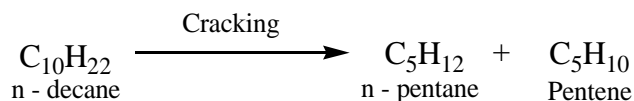
S.No	Name of the fraction	Constituents	Temperature
1	Uncondensed gases	$\text{CH}_4 - \text{C}_4\text{H}_{10}$	0-30 °C
2	Impure gasoline	$\text{C}_5\text{H}_{10} - \text{C}_{10}\text{H}_{22}$	30-200 °C
	a) Petroleum ether	$\text{C}_5\text{H}_{12} - \text{C}_6\text{H}_{14}$	Up to 80 °C
	b) Gasoline (Petrol)	$\text{C}_6\text{H}_{14} - \text{C}_7\text{H}_{16}$	80-150 °C
	c) Solvent naphtha	$\text{C}_7\text{H}_{16} - \text{C}_{10}\text{H}_{22}$	150-200 °C
3	Kerosene	$\text{C}_{11}\text{H}_{22} - \text{C}_{16}\text{H}_{34}$	200-300 °C
4	Gas Oil	$\text{C}_{16}\text{H}_{34} - \text{C}_{18}\text{H}_{38}$	Above 300 °C
5	Heavy oil	a) Lubricating oil, grease	$\text{C}_{17}\text{H}_{36} - \text{C}_{20}\text{H}_{42}$
	b) Paraffin wax	$\text{C}_{20}\text{H}_{42} - \text{C}_{28}\text{H}_{58}$	
6	Residue (Asphalt or tar, Petroleum coke)	C_{30} and above	

The uncondensed gases are lower hydrocarbons, highly combustible and are used as domestic fuels. All other products including asphalt etc., are useful in industries and public purposes. The most important fraction is gasoline, commercially known as petrol is highly volatile, inflammable secondary liquid fuel with great demand in automobile and aviation internal

combustion engines. It is only available to 20% and is called as straight run petrol and is insufficient. The rest of 80% to meet the needs is produced by cracking or from synthesis.

8. Cracking

Cracking may be defined as the process of breaking and converting higher molecular weight long chain hydrocarbons having high boiling point to lower molecular weight hydrocarbons with low boiling point.



The middle and heavy fractions of petroleum distillation products are cracked to get petrol. The petrol made by cracking has far better characteristics than the 'straight-run' petrol, as far as internal combustion engine is concerned.

There are two methods of cracking in use: i) Thermal cracking ii) Catalytic cracking

8.1. Thermal Cracking

The heavy oils are subjected to high temperature and pressure, when the long chain hydrocarbon molecules break down to give smaller chain molecules of the paraffins, olefins with a little hydrogen. This process may be carried out either in 'liquid-phase' or in 'vapor-phase'.

a) **Liquid-phase thermal cracking:** The heavy oil or gas oil stock is cracked at a suitable temperature of 475-530°C under a pressure of 100kg/cm². The cracked products are then separated in a fractionating column. The yield is 50-60% and octane rating of the petrol produced is 65-70.

b) **Vapor-phase thermal cracking:** The heavy oil is first vaporized and then cracked at about 600-650°C and under a low pressure of 10-20kg/cm². This process is suitable only for those oils, which may be readily vaporized. It requires less time than the liquid-phase method and petrol obtained from vapor-phase cracking has better anti-knock properties. However it has poor stability than petrol from liquid-phase cracking.

8.2. Catalytic cracking

The quality and yield of gasoline produced by cracking can be greatly improved by using a suitable catalyst like aluminium silicate, Al₂SiO₅ or alumina, (Al₂O₃). The catalyst is specific in its activity.

Advantages:

1. The yield of petrol is higher.
2. The quality of petrol produced is better.
3. The heat required for cracking is derived from the coal embedded in the catalyst., hence no external fuel supply is required.
4. A much lower pressure of about 1-5 kg/cm² is needed in catalytic cracking.
5. The cracking process can easily be controlled, so the desired products can be obtained.

6. The evolution of by-product gases can be minimized, thereby the yield of desired petrol is increased.
7. The product of cracking contains a higher amount of aromatics and hence the petrol possesses better anti-knock characteristics.
8. Isomerization to branched-chain compounds (iso-paraffins) occurs, thereby better petrol is produced.
9. The product contains a very little amount of undesirable S because a major portion of it escapes out as H_2S gas during cracking.
10. The percentage of gum or gum-forming compounds is very low.
11. Catalysts are selective in their action and, therefore, they permit cracking of only the high-boiling hydrocarbons.
12. In presence of catalyst, cracking is more in naphthenic materials than of paraffinic. So the products of catalytic cracking are more paraffinic.
13. Decomposition of aromatics removes only the side chains, but none of the ring by itself is broken.

There are two methods of catalytic cracking . a) fixed bed b) moving bed

a) **Fixed-bed catalytic cracking:** The block diagram of the process is shown below:

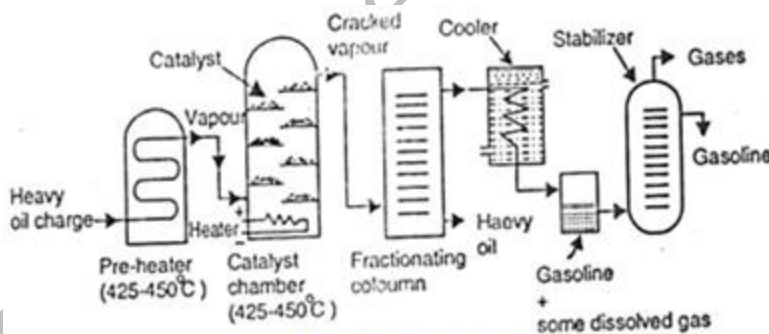


Fig.4. Fixed-bed catalytic cracking.

The oil vapors are heated in a pre-heater to cracking temperatures ($420-450^{\circ}C$) and then forced through a catalytic chamber containing artificial clay mixed with zirconium oxide maintained at $425-450^{\circ}C$ and 1.5 kg/cm^2 pressure. During their passage through the tower, about 40% of the charge is converted into gasoline and about 2-4% carbon is formed which gets adsorbed on the catalyst bed. The vapors produced are then passed through a fractionating column, where heavy oil fractions condense. The vapors are then led through a cooler, where some of the gases are condensed along with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a stabilizer, where the dissolved gases are removed and pure gasoline is obtained.

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

b) Moving-bed catalytic cracking: The solid catalyst is very finely powdered, so that it behaves almost as a fluid, which can be circulated in a gas stream. The vapors of cracking stock (gas oil, heavy oil, etc.) are mixed with fluidized catalyst and forced up into a large reactor 'bed' in which cracking of the heavier into lighter molecules occurs. Near the top of the reactor, there is a centrifugal separator (called cyclone separator), which allows the cracked oil vapors alone to pass on to the fractionating column, but retains all the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier, due to coating with carbon and settles down to the bottom, from where it is forced by an air blast to a regenerator (maintained at 600°C).

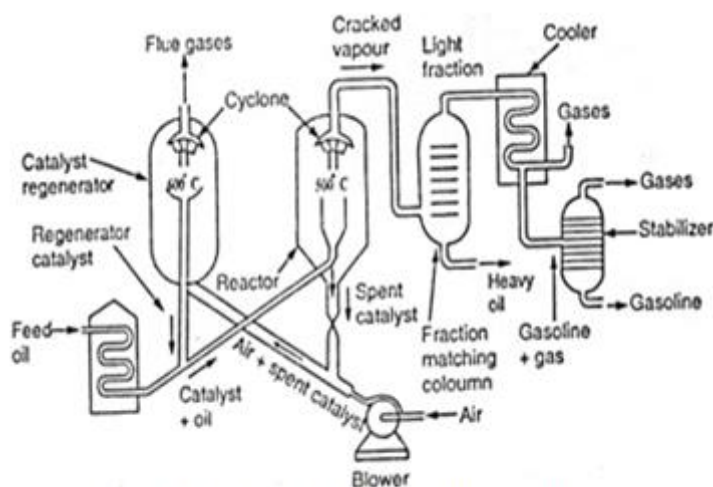


Fig. 5. Moving bed type catalytic cracking.

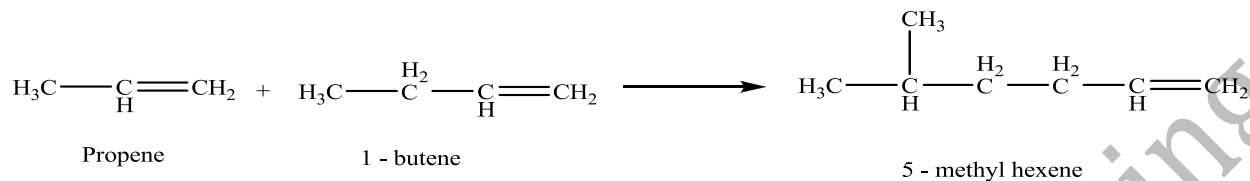
In the regenerator, carbon is burnt and the regenerated catalyst then flows through a stand-pipe for mixing with fresh batch of incoming cracking oil. At the top of the regenerator, there is a separator, which permits only gases (CO_2 , etc.) to pass out, but holds back catalyst particles. The catalyst particles are collected and carbon deposited on their surface is burnt off. The fresh catalyst regenerated is charged in to the catalyst chamber again.

9. Synthetic petrol

In view of the greater demand for petrol the synthetic methods gain importance. The following three methods are important synthetic processes for making petrol.

9.1. Polymerization: this method is opposite to cracking. The gases obtained as a by-product from cracking of heavy oils, etc., contain olefins (like ethylene, propene and butanes) and alkanes (such as methane, ethane, propane and butane). When this gaseous mixture is subjected to high pressure and high

temperature, with or without the presence of catalyst, they polymerizes to form higher hydrocarbons, resembling gasoline, called as polymer gasoline.



The polymerization is of two types:

- i) **Thermal polymerization:** In this process the polymerization of cracked gases is carried out at 500-600 °C and 70-350 kg/cm² pressure. The product is gasoline and gas oil mixture which are separated by fractionation.
- ii) **Catalytic polymerization:** This is carried out in presence of catalyst like phosphoric acid. In this case, lower temperature of 150-200°C is employed. Products are gasoline and un-polymerized gases. The latter is separated and recycled for polymerization.

9.2. Fischer-Tropsch method: Water gas (CO+H₂), produced by passing steam over preheated (at 1200 °C) hard coke, is mixed with hydrogen. The gas is purified by passing through Fe₂O₃ (to remove H₂S) and then into a mixture of Fe₂O₃+ Na₂CO₃ (to remove organic sulphur compounds). The purified gas is compressed to pressure of 30 atmospheres and then led through a convertor containing a catalyst, which is a mixture of 100 parts of cobalt, 5 parts of thoria, 8 parts of magnesia, and 200 parts of keiselguhar-earth, maintained at about 200-300°C. A mixture of saturated and unsaturated hydrocarbons results:

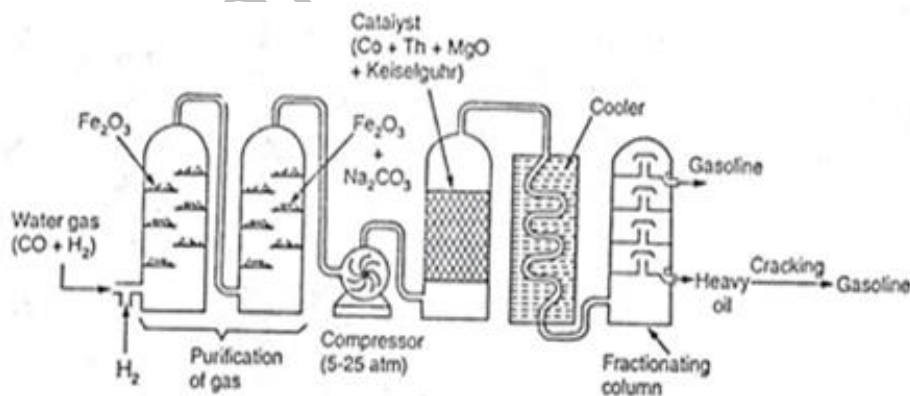
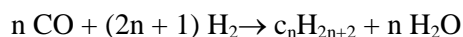
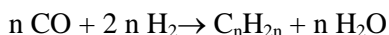


Fig. 6. Fisher-Tropsch method.



The reaction is exothermic as such the hot 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: (i) gasoline, and (ii) high-boiling heavy oil. The heavy oil is reused for cracking to get more gasoline.

9.3. Bergius process: 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). The paste is heated in a converter with hydrogen at 450°C and under a pressure 200-250 atm for about $1\frac{1}{2}$ hours, during which hydrogen combines with coal to form saturated hydrocarbons. They decompose at prevailing high temperature and pressure to yield low boiling liquid hydrocarbons. The released gases from the reaction vessel are led to condenser, where a liquid resembling that of crude oil is obtained, which is then fractionated to get: i) gasoline, ii) middle oil, and iii) heavy oil. The latter are used again for making paste with fresh coal dust. The middle oil is hydrogenated in vapor-phase in presence of a solid catalyst to yields more gasoline. The yield of gasoline is about 60% of the coal dust used.

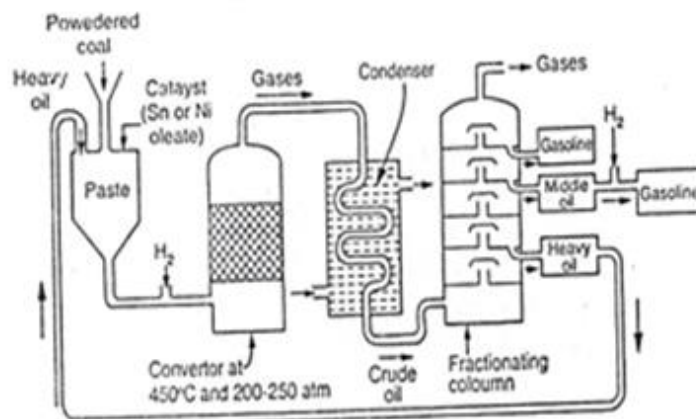


Fig. 7. Bergius process of hydrogenation of coal to gasoline.

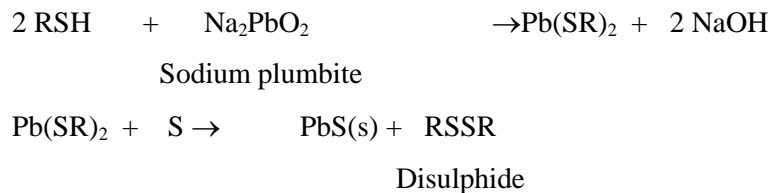
10. Refining of gasoline

The straight-run gasoline (obtained either from fractionation of crude petroleum or by synthesis) contains some undesirable unsaturated straight-chain hydrocarbons and sulphur compounds. The former gets oxidized and polymerized, thereby causing gum and sludge formation on storing. Sulphur compounds lead to corrosion of internal combustion engine. For this purpose, refining of petrol is necessary.

Characteristics of an ideal gasoline:

- 1) It must be cheap and readily available. It must burn completely and produce no corrosion, etc., in the parts of engine on combustion. It must have a high calorific value.
- 2) It should mix readily with air and afford uniform manifold distribution, i.e., it should easily vaporize.
- 3) It must be a knock-resistant. It should not pre-ignite easily.
- 4) It should not tend to decrease the volume efficiency of the engine.

10.1. Refining: The sulphur compounds are, generally, removed by treating gasoline with an alkaline solution of sodium plumbite with controlled addition of S. This refining process (called ‘sweetening’) converts sulphur compounds into disulphides (Doctor’s process).



The solid PbS is removed by filtration. Since disulphides in gasoline are also objectionable, disulphides, so-formed are extracted with a suitable solvent.

1. Olefins and coloring matter of gasoline are, usually, removed by percolating gasoline through ‘fuller’s earth’ (clay type material containing high magnesium oxide content), which adsorbs preferentially only the colors and olefins.
2. After the refining of gasoline, some inhibitors are added. They retard the oxidation reactions, thereby improving storing qualities of gasoline.

Even after refining, the gasoline does not have good combustion qualities and it is generally blended suitably with other fractions produced by catalytic cracking processes to meet the required specifications.

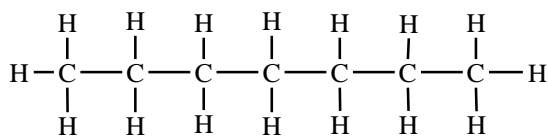
10.2. Knocking: A mixture of gasoline vapor and air is used as a fuel in an internal combustion engine. The combustion reaction is initiated by a spark in the cylinder, flame is spread rapidly and smoothly through the gaseous mixture. The expanding gas drives the piston down the cylinder.

The ratio of the gaseous volume in the cylinder at the end of the suction stroke to the volume at the end of the compression stroke of the piston is known as “compression ratio”. The efficiency of an internal combustion engine increases with the increase in the compression ratio which depends on the nature of the constituents present in the gasoline used. In certain circumstances, the rate of oxidation becomes so large that the last portion of the fuel – air mixture gets ignited instantaneously, producing an explosive rattling due to pre-ignition, known as ‘knocking’. The knocking results in the loss of efficiency of the engine.

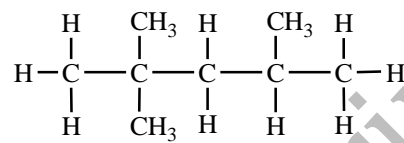
The knocking tendency of the hydrocarbons have the following order: straight chain paraffin > branched chain paraffin (iso paraffins) > olefins > cyclo paraffin (naphthalenes) > aromatics

10.3. Octane Number: The extent of knocking of petrol is measured by octane number. It was found that n-heptane knocks very badly and hence its anti-knock value has arbitrarily fixed as zero. On the other hand, iso-octane (2,2,4 – trimethyl pentane), gives very little knocking, so its anti-knocking value has been given as ‘100’. Thus octane number (or rating) of a gasoline (or any other internal combustion engine fuel) is the percentage of iso-octane in a mixture of iso-octane and n – heptane, which matches the

fuel under test in knocking characteristics. An '80 – octane' fuel has the same combustion characteristics as an 80:20 mixture of iso-octane and n – heptane. Hence higher the octane number greater is its anti-knocking property.



n-heptane
(Octane number = 0)



iso-octane
(2,2,4 - trimethyl pentane)
(Octane number = 100)

10.4. Improvement of anti-knock characteristics of a fuel: The octane number of fuels can be raised by the addition of materials such as tetra ethyl lead (C_2H_5)₄Pb or TEL, and diethyl telluride, (C_2H_5)₂Te, etc. Generally in motor spirit (or motor fuel) about 0.5mL and in aviation fuels, about 1.0 to 1.5mL of TEL per litre of petrol are added.

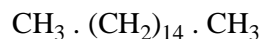
TEL is converted into a cloud of finely divided lead oxide particles in the cylinder and these particles react with any hydrocarbon peroxide molecules formed, thereby slowing down the chain oxidation reaction and decreasing the chances of any pre-ignition. However, deposit of lead dioxide is harmful to the engine life as well as causing environmental pollution.

An alternative method of increasing the octane number of petrol is to add high octane compounds like iso-pentane, iso-octane, ethyl benzene, isopropyl benzene, methyl tertiary butyl ether (MTBE) etc., to the petrol. MTBE is more preferred, as it contains oxygen in the form of ether group and supplies oxygen for the combustion of petrol and the extent of peroxy compound formation is reduced. Unleaded petrol is one where the enhancement of octane rating is accomplished without the addition of lead compounds.

10.5 Diesel engine fuels: In a diesel engine, fuel is exploded not by the spark ignition, but by the application of high temperature and pressure. Diesel engine fuels consist of longer chains hydrocarbons than fuels used in internal combustion engine. The main characteristic of this fuel is that it should ignite easily below compression temperature and there should be a short induction lag.

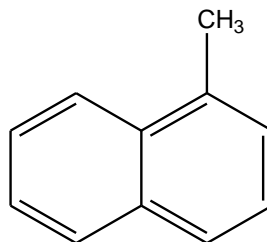
The suitability of diesel fuel is determined by its **cetane value (or cetane number)**, which is the percentage of hexa-decane in a mixture of hexa-decane and 2 – methyl naphthalene, which has the same ignition characteristics as the diesel fuel in use.

The cetane number of a diesel fuel can be increased by addition of small quantity of certain 'pre-ignition dopes' like ethyl nitrite, isoamyl nitrite, acetone peroxide, etc.,



n-hexa-decane
(Cetane)

Anti - knocking value = 100



Methyl naphthalene

Anti - knocking value = 0

Cetane number of a fuel depends on the nature and composition of its hydrocarbon. Ignition quality order among hydrocarbon constituents of a diesel fuel is as follows:

n-alkanes > naphthalene > alkenes > branched alkanes > aromatics

Hence it can be concluded that a good petrol is a bad diesel and vice – versa.

11. GASEOUS FUELS

The gaseous fuels are most preferred for industrial and domestic fuel needs. It is because:

1. They can be conveyed easily through pipes, eliminating manual labour transportation.
2. They have low ignition temperature, high heat content, low ash content and high calorific values.
3. They can be burnt without heat loss and can be completely combusted without pollution.
4. They burn in slight excess of air supply due to uniform mixing of air and fuel.

However they have the following disadvantages:

1. They require very large tanks for their storage.
2. They are highly inflammable.
3. Their cost is very high when compared to solid and liquid fuels.

11.1. Liquefied Petroleum Gas (LPG): It is a bottled gas or refinery gas obtained as a by – product, during the cracking of heavy oil from natural gas. It consists of hydrocarbons of such volatility that they can exist under atmospheric pressure but can be readily liquefied under pressure. The main constituents are n-butane, iso – butane, butene and propane, with little or no propene and ethane. It is dehydrated, desulphurized and contains traces of odorous substances (mectaptans) to give warning of gas. Its calorific value is 27,800 Kcal/m³.

Uses: The largest use of LPG at present is as a domestic fuel, motor fuel and industrial fuel.

Advantages of LPG over other gaseous fuels:

1. It has high efficiency and heating rate. The calorific value is roughly three times more than the natural gas and seven times than that of coal gas.
2. It is completely combustible without smoke.
3. It can be easily stored and has flexibility to control and portability.
4. It is advantageously used in engines working under high compression ratio.

Advantages of LPG over gasoline as motor fuel

1. It is cheaper to gasoline. And highly knock resistant.
2. It gives better manifold distribution and mixes easily with air.
3. It has less contamination and increases the life of an engine.

Disadvantages of LPG over gasoline as motor fuel

1. It has of faint odour, hence its leakage cannot be detected easily.
2. It has to be handled under pressures.
3. Its octane number is quite low and response to blending is very poor.

11.2. NATURAL GAS

It is obtained from the petroleum wells dug in the oil – bearing regions. When it occurs along with petroleum in oil wells, it is known as “wet gas” and when associated with crude oil, it is called “dry gas”. The main composition of natural gas is methane (70 - 90%), ethane (5 – 10%), hydrogen (3%), and the residual gases are CO and CO₂. its calorific value varies from 12,000 to 14,000 kcal/m³. The major impurities are water, dust, H₂S, CO₂, N₂ and heavier liquefiable hydrocarbons (propane, butane, butane, etc).

Uses

1. It is an excellent domestic fuel and can be conveyed through very long distances in pipes.
2. It is used in the manufacture of synthetic chemicals by synthetic processes.
3. It is also used a raw material for the manufacture of carbon black.
4. It is used in the manufacture of synthetic proteins (fermentation of methane).

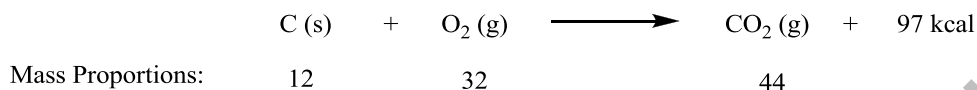
11.2 COMPRESSED NATURAL GAS (CNG)

It is the natural gas compressed to a high pressure of about 1000 atmospheres. A steel cylinder containing 15 kg of CNG contains about 20 m³ of natural gas at 1 atmosphere pressure. It is used as a substitute for petrol and diesel in automobiles. It causes comparatively less pollution as it does not evolve any gases containing sulphur and nitrogen. It is also used as a fuel for power generating diesel generators. It is a preferred fuel over LPG because:

1. It is a much safer fuel, since it ignites at much higher temperature than gasoline and diesel.
2. It is lighter, mixes with air easily and has narrow range of flammability.
3. It does not contaminate with lubricating oils and thus increases the life of internal combustion engine. It requires more space for storage and has calorific value 900KJ/mole.
4. The operating cost of CNG is much lower compared to gasoline.
5. Combustion of CNG leads to lesser CO emissions than gasoline.

12. COMBUSTION: Combustion is rapid oxidation of an element or compound with release of heat or light or both and hence the temperature rises considerably. The main elements which undergo combustion are carbon, hydrogen and sulphur.

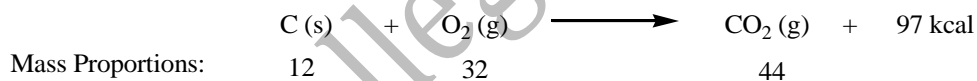
For example, combustion of carbon in oxygen:



For proper combustion, the substance must be brought to its kindling or ignition temperature. The ignition temperature is defined as “the minimum temperature at which the substance ignites and burn without further addition of heat from outside”. The percentage of CO₂ represents complete combustion of carbon present in the fuel. Presence of CO represents incomplete combustion. During combustion of a fuel, the oxygen in it will form water with hydrogen present in the fuel. Any excess hydrogen present will undergo combustion. The extent of combustion and the efficiency of a fuel can be determined by the analysis of flue gases coming out. Orsat’s apparatus is used for the analysis of flue gases.

12.1. CALCULATION OF QUANTITY OF AIR REQUIRED FOR COMBUSTION: The amount of air (oxygen) required for the combustion of a unit quantity of a fuel is calculated by following certain elementary principles:

1. “Substances always combine in definite proportions and these proportions are determined by molecular masses of the substances involved and the products formed”. In the following equation



When carbon combine with oxygen to form carbon dioxide, mass proportions of carbon, oxygen and carbon dioxide formed are 12: 32: 44 respectively.

2. 22.4 L or (22,400mL) of any gas at STP (i.e., at 0°C and 760 mm of Hg pressure) has a mass equal to one mole of the gas. Thus 22.4 L of CO₂ at STP will have a mass of 44g (mass of 1 mole of CO₂ gas).
3. Air contains 21% of oxygen by volume and mass per cent of oxygen in air is 23. This means that 1kg of oxygen is supplied from 4.35kg of air. Similarly 1 m³ of oxygen is supplied from 4.76m³ of air.
4. Molecular mass of air is taken as 28.94 g mol⁻¹ on average.
5. Minimum oxygen required = Theoretically calculated O₂ required – O₂ present in the fuel
6. Minimum oxygen required shall be calculated assuming complete combustion. If the combustion products contain CO and O₂, then excess O₂ is found by subtracting the amount of O₂ required to burn CO to CO₂.

- The mass of dry flue gases formed shall be calculated by balancing the carbon in the fuel and carbon in the flue gases.
- The mass of any gas can be converted to its volume at certain temperature and pressure by using the gas equation.

$$PV = nRT$$

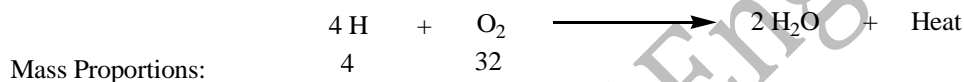
Where P = pressure of the gas in atmosphere.

V = volume of the gas in litres

n = No of moles of gas = No. of grams of gas /molar mass of the gas;

T = Temperature in Kelvin scale or absolute ($t^{\circ}\text{C} + 273.16$)

- The total amount of hydrogen is present, some is in the combined form as H_2O , known as non-combustible substances, which do not take part in combustion and the rest of hydrogen, known as available hydrogen takes part in the combustion process.



1 part of hydrogen combines chemically with 8 parts by mass of oxygen, so the available hydrogen is = Mass of hydrogen – (Mass of oxygen/8)

Theoretical amount of Oxygen required for complete combustion of 1 kg of solid or liquid fuel is

$$\left[\frac{32}{12} \times C + 8 \left(H - \frac{O}{8} \right) + S \right] \text{ kg}$$

Where C, H, S and O are the masses of carbon, hydrogen, sulphur and oxygen respectively per kg of fuel.

Since the percentage of oxygen in air by mass is 23, so the amount of air required theoretically for combustion of 1 kg of fuel

$$\frac{100}{23} \left[\frac{32}{12} \times C + 8 \left(H - \frac{O}{8} \right) + S \right] \text{ kg}$$

Problems on calculation of quantity of air required for combustion:

Worked out example 1

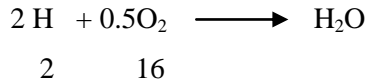
A sample of coal was found to contain: C = 80%; H = 5%; O = 1%; N = 2%; remaining being ash.

Calculate the amount of minimum air required for complete combustion of 1kg of coal sample.

Solution

1 kg of coal contains: C = 800g; H = 50g; O = 10g; N = 20g





$$\begin{array}{rcl}
 50\text{g (16/2)} & = & 400\text{g} \\
 \text{Total} & = & 2,546\text{g} \\
 \text{Less O in fuel} & = & 10\text{g} \\
 \text{Net O}_2 \text{ req.} & = & 2,536\text{g}
 \end{array}$$

Therefore, weight of air required = $2,536\text{g} (100 / 23) = 11,026\text{g} = 11.026 \text{ kg}$

Worked out example 2

A fuel is found to contain: C = 90%, H = 6.0%, S = 2.5%, O = 1.0% and ash = 0.5%. Calculate the amount of air required for the complete combustion of 1kg of fuel. If 25% excess air is used for combustion, calculate the amount of dry products in the flue gas.

Solution: 1kg of coal contains: C = 900g, H = 60g, S = 25g, O = 10g.

Therefore, Amount of air required for complete combustion of 1kg of coal

$$\left[900 \times \left(\frac{32}{12} \right) + 60 \left(\frac{16}{2} \right) + 25 \left(\frac{32}{32} \right) - 10 \right] \text{g} \times \left(\frac{100}{23} \right) = 12,587\text{g or } 12.587\text{kg}$$

Calculation of dry products, when 25% excess air is used

$$\text{Weight of CO}_2 = 900\text{g} \times (44/12) = 3,300\text{g}$$

$$\text{Weight of SO}_2 = 25\text{g} \times (64/32) = 50\text{g}$$

$$\text{Weight of N}_2 = 12,587\text{g} \times (77/100) \times (125/100) = 12,115\text{g}$$

$$\text{Weight of O}_2 = 10\text{g (of fuel)} + 12,587\text{g} \times (23/100) \times (125/100) = 3,626\text{g}$$

$$\text{Total weight of flue gas} = (3,300 + 50 + 12,115 + 3628)\text{g} = 19,093\text{g}$$

$$\text{Percentage of: } \text{CO}_2 = \frac{3,300 \times 100}{19,093} = 17.28\%$$

$$\text{SO}_2 = \frac{50 \times 100}{19,093} = 0.26\%$$

$$\text{N}_2 = \frac{12,115 \times 100}{19,093} = 63.34\%$$

$$\text{O}_2 = \frac{3,628 \times 100}{19,093} = 19.02\%$$

Worked out example 3

A producer gas has the following percentage composition by volume: CH₄ = 3.5%; CO = 25%; H₂ = 10%; CO₂ = 10.8%; N₂ = 52.7%. Calculate: (i) theoretical quantity of air required per m³ of the gas; (ii) percentage composition of products of combustion including water vapour formed; (iii) if 25% excess air is used, find percentage composition of the dry products of combustion; (iv) weight of dry flue gas formed by burning 1m³ of producer gas.

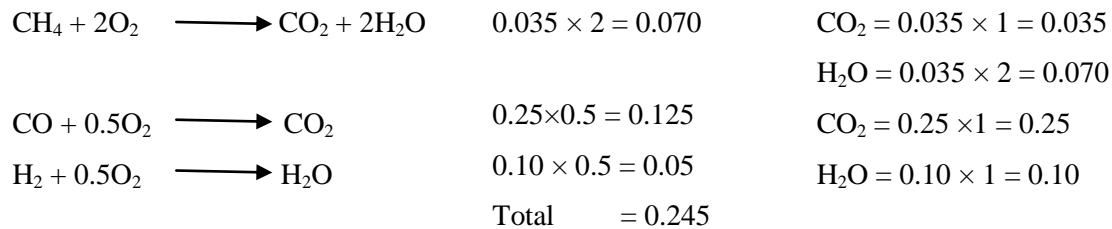
Solution

1 m³ of gas contains: CH₄ = 0.035m³; CO = 0.25m³; H₂ = 0.10m³; CO₂ = 0.108 m³; N₂ = 0.527m³

Combustion Reaction

Vol. of O₂ needed (m³)

Vol. of products (m³)



(i) Theoretical quantity of air required per m^3 of gas = $0.245 \text{ m}^3 \times (100/21) = 1.16 \text{ m}^3$

(ii) Calculation of volume of products of combustion:

$$\text{CO}_2 = (0.035 + 0.25) \text{ m}^3 + 0.108 \text{ m}^3 (\text{fuel}) = 0.393 \text{ m}^3$$

$$\text{H}_2\text{O} = (0.070 + 0.10) \text{ m}^3 = 0.170 \text{ m}^3$$

$$\text{N}_2 = 79 \% \text{ of } 1.16 \text{ m}^3 + 0.527 \text{ m}^3 (\text{of fuel}) = 1.072 \text{ m}^3$$

$$\text{Total volume of the products} = 2.003 \text{ m}^3$$

Calculation of percentage composition of products:

$$\text{CO}_2 = \frac{0.393 \times 100}{2.003} = 19.6\%$$

$$\text{H}_2\text{O} = \frac{0.170 \times 100}{2.003} = 8.48\%$$

$$\text{N}_2 = \frac{1.027 \times 100}{2.003} = 71.89\%$$

(iii) Calculations of dry products of combustion using 25% excess air:

$$\text{CO}_2 (\text{as calculated above}) = 0.393 \text{ m}^3 (\text{or } 393\text{L})$$

$$\begin{aligned} \text{N}_2 &= 79\% \text{ of minimum air used} \times (125 / 100) + 0.527 \text{ m}^3 \\ &= 1.16 \text{ m}^3 \times (79 / 100) \times (125 / 100) + 0.527 \text{ m}^3 = 1.15 \text{ m}^3 (\text{or } 1,150\text{L}) \end{aligned}$$

$\text{O}_2 = 25\% \text{ of minimum oxygen required}$

$$= 0.245 \text{ m}^3 \times (25 / 100) = 0.06 \text{ m}^3 (\text{or } 60\text{L})$$

$$\text{Total volume of dry products} = 1.603 \text{ m}^3 (\text{or } 1,603\text{L})$$

Calculation of percentage of dry products of combustion:

$$\text{CO}_2 = \frac{0.393 \times 100}{1.603} = 24.5\%$$

$$\text{N}_2 = \frac{1.027 \times 100}{1.603} = 71.7\%$$

$$\text{O}_2 = \frac{0.06 \times 100}{1.603} = 3.74\%$$

(iv) Weight of dry products of combustion obtained by burning 1 m^3 of gas:

$$= 393\text{L} \times \left(\frac{44\text{g}}{22.4\text{L}}\right) + 1,150.4\text{L} \times \left(\frac{28\text{g}}{22.4\text{L}}\right) + 60\text{L} \times \left(\frac{32\text{g}}{22.4\text{L}}\right)$$

$$= (771.96\text{g} + 1,437.5\text{g} + 85.71\text{g}) = 2,295\text{g} = 2.295\text{kg}$$

13. Practice problems

13.1. Calculate the higher and lower calorific value of a coal sample containing 84% of carbon, 1.5% of sulphur, 0.6% of nitrogen, 5.5% of hydrogen and 8.4% of oxygen.

Answer: (I) 8,356 kcal/ kg, (II) 8,066 kcal / kg

13.2. A liquid fuel weighing 0.98g and containing 90.1% C, 8% H, have the following results in bomb calorimeter experiment.

Amount of water taken in calorimeter = 1,450 g

Water equivalent of calorimeter = 450 g

Rise in temperature of water = 1.8 °C

If latent heat of steam is 587 cal / g, calculate gross and net calorific value of fuel.

Answer: (i) 3,490 cal/g (ii) 3,097 cal/g

13.3. Calculate the gross and net calorific value of coal sample having the following composition:

C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.1% and ash = 4.4%.

Answer: GCV = 8,828kcal/kg, NCV = 8,458 kcal/kg

13.4. A gas has the following composition by volume: H₂ = 20%; CH₄ = 6%; CO = 22%; CO₂ = 4%; O₂ = 4% and N₂ = 44%. 20% excess air is used. Find the weight of air actually supplied per m³ of this gas. Molecular weight of air = 28.97.

Answer: 2,143g

13.5. A producer gas has the following composition by volume: CO = 30%; H₂ = 12%; CO₂ = 4%; CH₄ = 2% and N₂ = 52%. What will be the composition of dry flue gas, if 50% excess air was used for burning 100m³ of the gas.

Answer: CO₂ = 14.1%; N₂ = 79.8%; O₂ = 5.1%.

13.6. A gaseous fuel containing; H₂ = 10%; CH₄ = 30%; C₂H₂ = 15%; C₄H₁₀ and C₂H₆ = 20% by volume was burnt in 10% excess of theoretical air by mass required for complete combustion. Find out the analysis of dry products of combination.

Answer: CO₂ = 40.16%; N₂ = 58.43%; O₂ = 1.41%.

Assignment Questions

1. How are fuels classified? Explain with examples
2. Briefly explain the important characteristics of a good fuel.
3. Compare the advantages and limitations of solid, liquid and gaseous fuels
4. What is proximate analysis of coal? What is the significance of the analyses
5. Write a brief account of ultimate analysis of coal. What is its significance
6. Define calorific value of a solid fuel. How it is determined experimentally using bomb calorimeter.
7. What do you understand by high and low calorific values of a fuel? How it is determined by Junker's calorimeter? Describe with a neat labeled diagram.
8. What is pulverization of coal? What are the advantages and disadvantages of pulverized coal?
9. Describe the production of metallurgical coke by beehive oven process.
10. Briefly explain the production of coke by Otto Hoffman's process.
11. What are the byproducts that are recovered from coke-oven gas and how they are recovered?
12. Compare the temperature and high temperature carbonization of coal.
13. Describe the production of petrol from water gas.
14. What are the different varieties of crude oil generally obtained?
15. What is cracking of oil? How is this useful in petroleum industry?
16. Hydrogenation of coal is a source of petrol. Describe how petrol can be produced from this source.
17. Explain knocking in IC engines using petrol as fuel.
18. What are the merits and demerits of liquid fuels?
19. Define Cetane Number of a fuel.
20. Explain how catalytic cracking of oil is better than thermal cracking to produce petrol.
21. Explain the term octane number of the fuel
22. What are the advantages and limitations of the liquid fuels compared to solid fuels?
23. What is cracking of oil and how this process is useful in petroleum industry?
24. What is Cetane number and how it differs from octane number.
25. Explain briefly the fractional distillation of petroleum.
26. Write notes on anti-knocking agents that are used with petrol.
27. Explain the difference in knocking between petrol engines and diesel engines.
28. Describe the Fischer – Tropsch process for the production of synthetic petrol.
29. What is cracking of oil. Explain the moving bed catalytic cracking method of oil.

30. Write short notes on
- Refining of gasoline
 - Reforming of gasoline
 - Gasoline from polymerization.
31. What is LPG? What are the advantages of LPG over other fuel gases.

Problems:

32. A bomb calorimeter, whose water equivalent is 144 gm, was filled with 1458 gm of water. When 0.945 gm of coal was burnt in it the temperature of water rose by 5.95 °C calculate the HCV of the fuel. If the hydrogen percentage in the fuel was 7 calculate LCV of the fuel (latent heat of condensation of steam is 587 cal/gm)
33. Calculate the gross and net calorific values of coal having the following composition:
Carbon: 87% Hydrogen: 5% Sulphur : 0.5% Nitrogen : 0.5% Oxygen : 3% Ash :4% ;
latent heat of steam : 587 cal / gram.
34. Calculate the calorific value of the coal given the following data:
Wt. of the fuel burnt: 0.945 g Initial temp. : 13.25 °C Final temp.: 19.2 °C
Water in the calorimeter: 1458 g. Water equivalent of the calorimeter: 144 g.
35. Calculate the gross and net calorific value of coal having the following composition:
Carbon: 85% Hydrogen: 8% Sulphur: 1% Nitrogen: 2% Oxygen: 2% Ash: 2% and Latent heat of steam: 587 cals per gram.
36. A sample of coal weighing 1.232 g was heated at 105 °C for an hour and the residue weighed 1.186 g. The residue was then heated in a muffle furnace at 940 °C for seven minutes and the residue now weighed 1.126 g. Finally the residue was heated in presence of air at 750°C till a constant weight (0.080 g.) was attained. Calculate the results and explain what conclusions you can draw.
37. A liquid fuel weighing 0.98 g gave the following results in bomb calorimetric experiment:
Amount of water taken in the calorimeter: 1450 g
Water equivalent of calorimeter: 450 g
Raise in temperature of water: 1.8 °C.
Latent heat of steam: 587 cals. per g
If the coal sample contains 8% hydrogen, calculate the HCV and LCV of the fuel.
38. A coal sample weighing 1.98 g on heating at 110 °C for one hour left a residue of 1.78 g. This residue was heated in a suitable crucible with a suitable lid at 950 °C for exactly seven minutes and the residue weighed 1.59 g. This residue was heated in presence of air till a constant weight was obtained. This residue weighed 0.231 g. Calculate the proximate analysis of the coal.

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