

## Part B

### Unit - V

#### Chemical Fuels and Photovoltaic cells

*Introduction, Classification of chemical fuels, Calorific value – High and Low calorific values, Determination of calorific value –solid or liquid fuel using Bomb calorimeter, Numerical problems. Petroleum – Cracking by fluidized catalytic cracking process, Reformation of petrol, Octane and Cetane numbers. Knocking – mechanism and harmful effects. Antiknocking agents – TEL, Catalytic converters – Principle and working, Unleaded petrol, Power alcohol and Biodiesel (synthesis by transesterification and advantages). Photovoltaic cells – Production of solar grade silicon, Doping of silicon, Construction and working of photovoltaic cell, Advantages.*

#### Introduction:

Energy is the primary and most universal measure of all kinds of work by human beings and nature. Every thing what happens in the world is the expression of flow of energy in one of its forms. Most people use the word energy for input to their bodies or to the machines and thus think about crude fuels and electric power.

Energy is an important input in all sectors of any country's economy. The standard of living of a given country can be directly related to per capita energy consumption. Energy crisis is due to the two reasons; firstly that the population of the world has increased rapidly and secondly the standard of living of human beings has increased. If the present trend is continues, the world in the 2050 AD will be more crowded and the energy consumption would have increased exponentially. The discussion on energy, has got much importance as the conventional sources mainly fossil fuels are depleting rapidly. In this unit, the discussion is mainly about fossil fuels and solar energy.

*“Chemical fuel is a combustible substance which on combustion in presence of air or oxygen liberates large amount of energy in the form of heat that can be used economically for both industrial and domestic purposes.”* The energy released during combustion of a chemical fuel is due to the formation of products of lower heat content than that of the fuel itself.



The common examples of chemical fuel are wood, coal, charcoal, kerosene, petrol, diesel, crude oil, coal gas, water gas etc.

## CLASSIFICATION OF CHEMICAL FUELS

Chemical (Fossil) Fuels may be classified on the basis of their occurrence

1) Primary or natural fuels are those, which occur in nature and are used without processing.

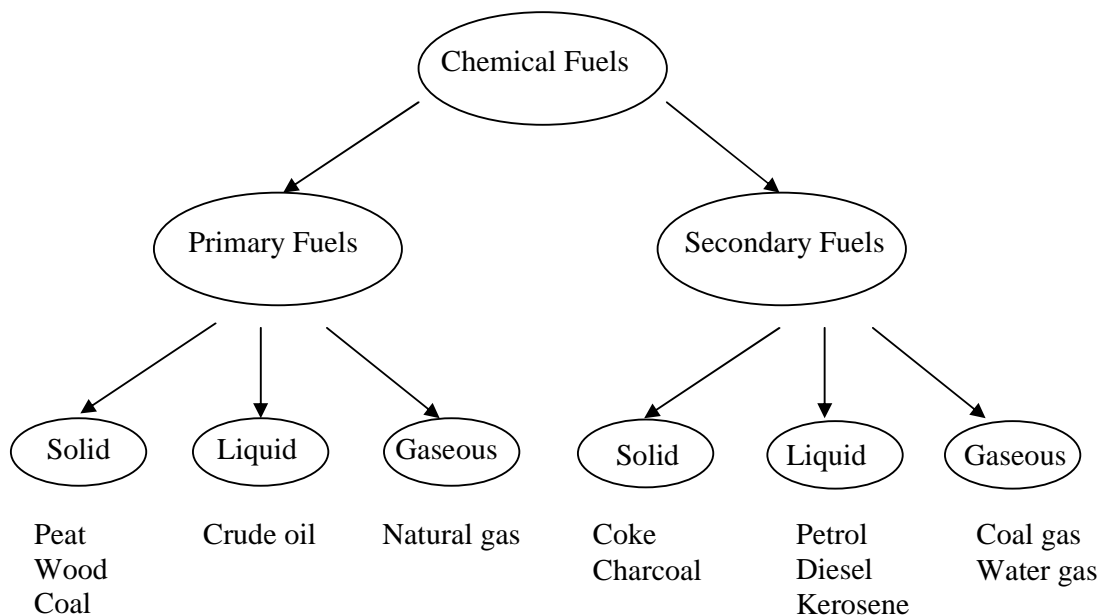
Ex: Wood, coal, crude oil, peat, Natural gas etc

2) Secondary fuels are those, which are derived from primary fuels.

Ex: Coke, Charcoal, kerosene, diesel, petrol, LPG etc.

Chemical Fuels are further classified on the basis of their physical state like solid, liquid or gas.

A schematic picture of classification of fuel is shown in figure 5.1.



**Figure 5.1 Classification of Chemical fuels**

## CALORIFIC VALUE

*Calorific value of a fuel is defined as the amount of heat liberated when unit mass or unit volume of fuel is burnt completely in presence of excess of air. The quality of the fuel is measured in terms of its calorific value. Higher the calorific value better is the fuel.*

S.I. unit of calorific value for solid or liquid fuels is kJ/kg and kJ/m<sup>3</sup> for gaseous fuels.

### **Higher or Gross Calorific value (GCV):**

Usually, all fuels contain hydrogen in their molecular structure. During the process of combustion hydrogen is converted into steam. If the products of combustion are cooled to room temperature, the latent heat of condensation of steam also gets included in the measured heat, which is called gross or higher calorific value.

The gross calorific value may be defined as *“the amount heat liberated, when unit mass or unit volume of fuel is burnt completely in presence of excess of air and the products of combustion are cooled to room or ambient temperature.”*

### **Lower or Net Calorific value (NCV):**

Practically, the products of combustion of any fuel are not condensed to room temperature instead they are allowed to escape. The steam produced during the combustion escapes with exhaust gases. So, the latent heat of steam is not included in the measured heat. Hence, net calorific value is always less than the gross calorific value.

The net calorific value may be defined as *“the amount of heat liberated, when unit mass or unit volume of fuel is burnt completely in presence of excess of air and the products of combustion are allowed to escape”*.

$$\text{NCV} = \text{GCV} - \text{latent heat of steam}$$

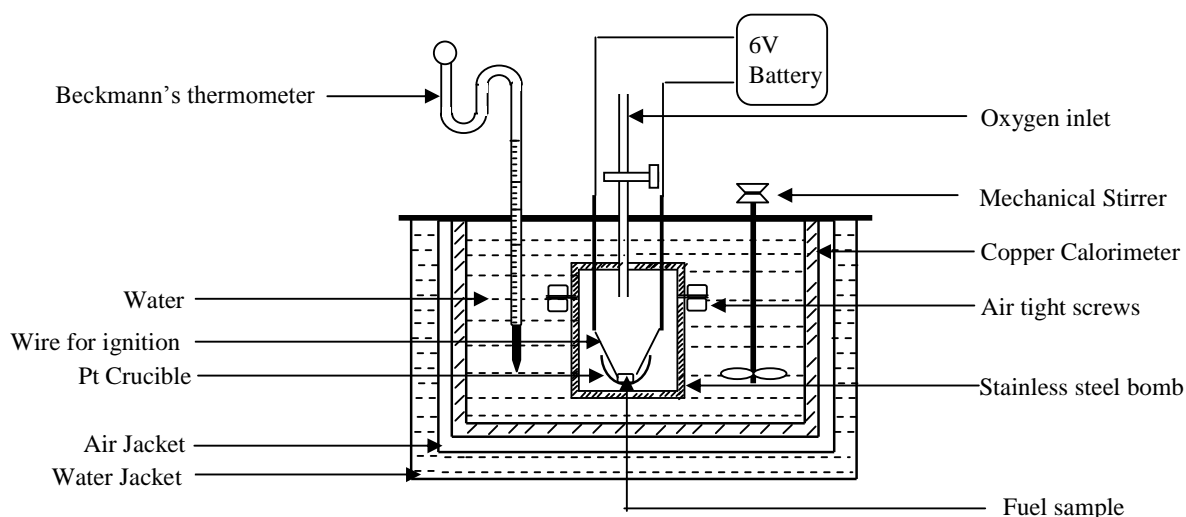
### **Characteristics of a good fuel:**

1. A good fuel should have high calorific value.
2. It should have moderate ignition temperature. Ignition temperature is the lowest temperature to which the fuel must be pre heated so that it starts burning smoothly. Low ignition temperature is dangerous for storage and transportation of the fuel and the high ignition temperature causes difficulty in igniting.
3. The fuel should have low moisture content. The presence of moisture reduces the calorific value.
4. It should have low content of non-combustible matter. The presence of non-combustible matter reduces the calorific value.
5. It should have moderate velocity of combustion.
6. The products of combustion should not be harmful.
7. A good fuel should burn efficiently without smoke.
8. A good fuel should be easy to store, handle and transport at a low cost.
9. Combustion should be easily controllable.

## Determination of calorific value of solid or liquid fuel by using bomb calorimeter

**Principle:** The amount of heat liberated by burning a sample of fuel in presence excess of oxygen or air is equal to the amount heat absorbed by the surrounding water and the calorimeter.

**Construction:** The experimental set up consists of a cylindrical stainless steel bomb (vessel of 500 cm<sup>3</sup> capacity) with an air tight screw and an inlet for oxygen. The bomb has a platinum crucible with magnesium ignition wires to ignite the fuel. The bomb is immersed in a well insulated copper calorimeter containing water. The copper calorimeter is provided with a mechanical stirrer for dissipation of heat and a Beckmann thermometer to read the temperature accurately.



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Fig. 5.2 Bomb Calorimeter

**Working:** A known mass (about 0.5 to 1.0 × 10<sup>-3</sup> kg) of the given fuel is taken in a clean platinum crucible. The bomb lid is tightly screwed and bomb is filled with oxygen at a pressure of 25 - 30 atmosphere. The bomb is then lowered into copper calorimeter, containing a known mass of water. The water is kept in constant agitation by the mechanical stirrer. The initial temperature of the water is recorded. The fuel is ignited by passing electric current using a 6 V battery through ignition wires. The fuel burns and the heat liberated is absorbed by the water and calorimeter. The temperature of water rises and the final temperature is recorded.

The water equivalent of the calorimeter is determined by burning a fuel such as benzoic acid or salicylic acid whose calorific value is known.

### Observations and Calculations:

Let  $m$  = mass of fuel sample taken in the crucible  
 $W_1$  = mass of water taken in the calorimeter  
 $W_2$  = water equivalent of calorimeter  
 $t_1$  °C = initial temperature of water  
 $t_2$  °C = final temperature of water  
 $s$  = specific heat of water

Heat liberated by burning the fuel =  $m \times \text{GCV}$

Heat absorbed by water and calorimeter =  $(W_1 + W_2) \times s \times (t_2 - t_1)$

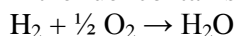
But, heat liberated by burning the fuel = heat absorbed by water and calorimeter

$$m \times \text{GCV} = (W_1 + W_2) \times s \times (t_2 - t_1)$$

$$\text{GCV} = \frac{(W_1 + W_2) \times s \times (t_2 - t_1)}{m} \quad \text{kJ kg}^{-1}$$

### Calculation of Net calorific value:

If the fuel contains H % of hydrogen



2 g of hydrogen produces 18 g of water

1 g of hydrogen produces 9 g of water

Water formed by 1 g of fuel =  $9 \times \text{H}/100 = 0.09 \times \text{H} \text{ g}$

Latent heat of steam =  $587 \times 4.187 \text{ kJ kg}^{-1}$

Latent heat of steam formed =  $0.09 \times \text{H} \times 587 \times 4.187 \text{ kJ kg}^{-1}$

$\text{NCV} = \text{GCV} - \text{latent heat of steam formed}$

$$\text{NCV} = \text{GCV} - 0.09 \times \text{H} \times 587 \times 4.187 \quad \text{kJ kg}^{-1}$$

### Numericals:

1) 0.945 g of fuel on complete combustion in excess of oxygen increased the temperature of water in a calorimeter from 13.25 to 19.2 °C. The mass of water in the calorimeter was found to be 1458 g. Calculate the gross calorific value of the fuel, if the water equivalent of calorimeter is 144 g. (VTU, April 2000)

#### Solution:

Weight of the fuel =  $m = 0.945 \text{ g} = 0.945 \times 10^{-3} \text{ kg}$

Weight of water =  $W_1 = 1458 \text{ g} = 1458 \times 10^{-3} \text{ kg}$

Water equivalent of calorimeter =  $W_2 = 144 \text{ g} \times 10^{-3} \text{ kg}$

Specific heat of water =  $4.187 \text{ kJ kg}^{-1} \text{ K}^{-1}$

$t_2 - t_1 = (273 + 19.2) - (273 + 13.25) = 5.95 \text{ K}$

$$\begin{aligned} \text{GCV} &= \frac{(W_1 + W_2) \times s \times (t_2 - t_1)}{m} \\ &= \frac{(1458 \times 10^{-3} + 144 \times 10^{-3}) \times 4.187 \times 5.95}{0.945 \times 10^{-3}} \\ &= 42232.87 \text{ kJ kg}^{-1} \end{aligned}$$

- 2) Calculate the gross calorific value and net calorific value of a sample of coal 0.5g of which, when burnt in a bomb calorimeter, raised the temperature of 1000g of water from 293 K to 296.4 K. The water equivalent of calorimeter is 350 g. The specific heat of water is  $4.187 \text{ kJ kg}^{-1}$ , latent heat of steam is  $257.2 \text{ kJ kg}^{-1}$ . The coal sample contains 93% carbon, 5% hydrogen and 2% ash.

**Solution:**

Weight of the fuel =  $m = 0.5 \text{ g} = 0.5 \times 10^{-3} \text{ kg}$

Weight of water =  $W_1 = 1000 \text{ g} = 1000 \times 10^{-3} \text{ kg}$

Water equivalent of calorimeter =  $W_2 = 350 \text{ g} \times 10^{-3} \text{ kg}$

Specific heat of water =  $4.187 \text{ kJ kg}^{-1} \text{ K}^{-1}$

$$t_2 - t_1 = 296.4 - 293 = 3.4 \text{ K}$$

$$\text{GCV} = \frac{(W_1 + W_2) \times s \times (t_2 - t_1)}{m}$$

$$= \frac{(1000 \times 10^{-3} + 350 \times 10^{-3}) \times 4.187 \times 3.4}{0.5 \times 10^{-3}}$$

$$= 38437 \text{ kJ kg}^{-1}$$

$$\text{NCV} = \text{GCV} - 0.09 \times H \times 587 \times 4.187$$

$$= 38437 - 0.09 \times 5 \times 2457.2$$

$$= 38437 - 1106$$

$$= 37331 \text{ kJ kg}^{-1}$$

3) A coal sample with 93% C, 5%  $\text{H}_2$  and 2% ash is subjected to combustion in a bomb calorimeter. Calculate the GCV and NCV given that, (VTU Aug 02)

Weight of the fuel =  $m = 0.95 \text{ g} = 0.95 \times 10^{-3} \text{ kg}$

Weight of water =  $W_1 = 2000 \text{ g} = 2000 \times 10^{-3} \text{ kg}$

Water equivalent of calorimeter =  $W_2 = 700 \text{ g} = 700 \times 10^{-3} \text{ kg}$

Specific heat of water =  $4.187 \text{ kJ kg}^{-1} \text{ K}^{-1}$

Rise in temperature,  $(t_2 - t_1)$  =  $2.8 \text{ K}$

Latent heat of steam =  $587 \times 4.187 \text{ kJ kg}^{-1}$

**Solution:**

$$\text{GCV} = \frac{(W_1 + W_2) \times s \times (t_2 - t_1)}{m}$$

$$= \frac{(2000 \times 10^{-3} + 700 \times 10^{-3}) \times 4.187 \times 2.8}{0.95 \times 10^{-3}}$$

$$= 33319.705 \text{ kJ kg}^{-1}$$

$$\text{NCV} = \text{GCV} - 0.09 \times H \times 587 \times 4.187$$

$$= 33319.705 - 0.09 \times 5 \times 2457.2$$

$$= 33319.705 - 1106$$

$$= 32213.705 \text{ kJ kg}^{-1}$$

4) Calculate the GCV and NCV of a coal sample from the following data:

(VTU Jan 2010)

Weight of the fuel =  $m = 0.98 \text{ g} = 0.98 \times 10^{-3} \text{ kg}$

Weight of water =  $W_1 = 2600 \text{ g} = 2600 \times 10^{-3} \text{ kg}$

Water equivalent of calorimeter =  $W_2 = 368 \text{ g} = 368 \times 10^{-3} \text{ kg}$   
 Specific heat of water =  $4.187 \text{ kJ kg}^{-1} \text{ K}^{-1}$   
 Rise in temperature,  $t_2 - t_1 = 2.8 \text{ K}$   
 Latent heat of steam =  $587 \times 4.187 \text{ kJ kg}^{-1}$   
 Percentage of hydrogen in coal sample = 5.8

**Solution:**

$$\begin{aligned} \text{GCV} &= \frac{(W_1 + W_2) \times s \times (t_2 - t_1)}{m} \\ &= \frac{(2600 \times 10^{-3} + 368 \times 10^{-3}) \times 4.187 \times 2.8}{0.98 \times 10^{-3}} \\ &= \mathbf{35505.76 \text{ kJ kg}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - 0.09 \times H \times 587 \times 4.187 \\ &= 35505.76 - 0.09 \times 5.8 \times 2457.2 \\ &= 35505.76 - 1282.95 \\ &= \mathbf{34222.81 \text{ kJ kg}^{-1}} \end{aligned}$$

5) The GCV of a sample of bituminous coal is  $36000 \text{ kJ kg}^{-1}$ . In an experiment 0.83 g of this coal was burnt under 1.2 kg of water in a bomb calorimeter. Due to combustion the temperature of water rose by  $3.92^\circ \text{C}$ . Calculate the water equivalent of calorimeter. (Specific heat water =  $4.2 \text{ kJ kg}^{-1} \text{ }^\circ \text{C}^{-1}$ ) (VTU Jan 2006)

**Solution:**

$$\begin{aligned} \text{GCV} &= \frac{(W_1 + W_2) \times s \times (t_2 - t_1)}{m} \\ 36000 &= \frac{(1.2 + W_2) \times 4.2 \times 3.92}{0.83 \times 10^{-3}} \\ (1.2 + W_2) &= 36000 \times 0.83 \times 10^{-3} / (3.92 \times 4.2) \\ W_2 &= 1.814 - 1.2 \end{aligned}$$

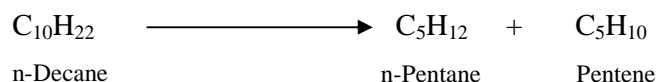
Water equivalent of calorimeter;  $W_2 = \mathbf{0.614 \text{ kg}}$

### **CRACKING OF PETROLEUM:**

Petroleum is derived from Greek words petra and oleum. Petra means rock and oleum means oil. Petroleum or crude oil is a dark coloured, viscous oily liquid found deep in the earth crust. It mainly consists of mixture of aliphatic and aromatic hydrocarbons. The fractionation of petroleum yields only 20% of gasoline. In order to meet the increasing demand for gasoline, it has become necessary to convert the long chain compounds into smaller fractions.

*“Cracking is a process in which long chain hydrocarbons of high molecular weight and high boiling point are broken down to smaller fragments of lower molecular weight and lower boiling point.”*

E.g.



There are two types of cracking,

- 1) Thermal cracking
- 2) Catalytic cracking

### Thermal Cracking:

In thermal cracking, the heavy oil fraction of petroleum is subjected to high pressure (5 – 10 Atmospheres) and temperature (about 600 – 700 °C). The cracked vapors are fractionated to get low molecular weight alkanes and alkenes.

### Catalytic Cracking

In this method, cracking is brought in the presence of a catalyst at very low temperature and pressure. The quality and yield of gasoline produced by cracking can be greatly improved by using a suitable catalyst like aluminium silicate or alumina.

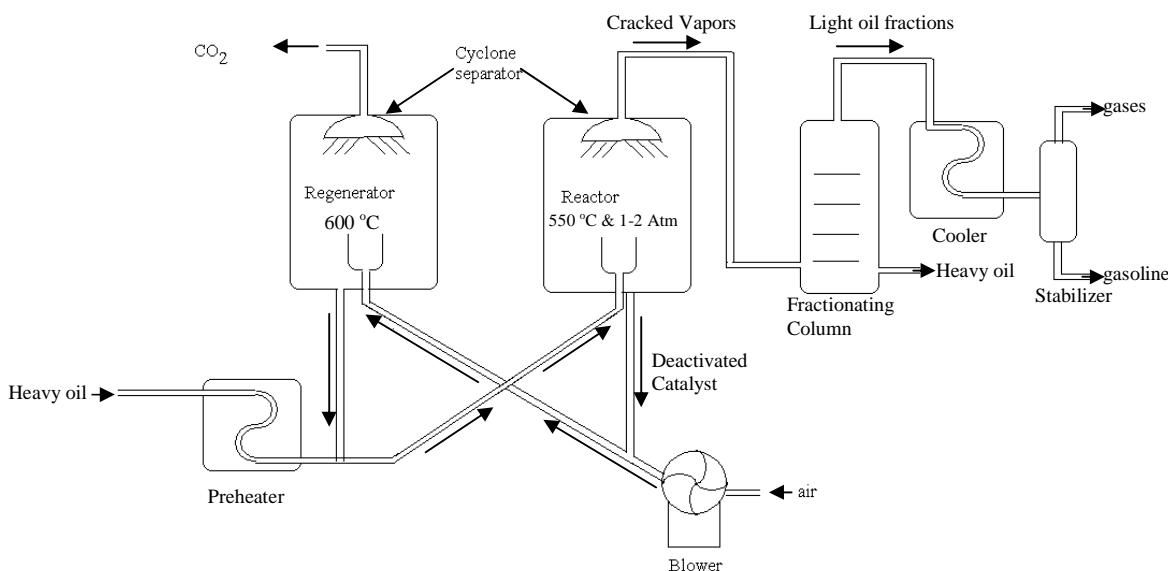
There are two types of catalytic cracking processes

- 1) Fixed bed catalytic cracking
- 2) Fluidized (Moving) bed catalytic cracking

### Fluidized (Moving) bed catalytic cracking

#### Working:

The solid catalyst is finely powdered, so that it behaves almost as a fluid, which can be circulated in gas stream. Heavy oil is vaporized by preheating to 400 – 500 °C. The vapors of heavy oil are mixed with fluidized catalyst and fed into a reactor in which cracking of heavy oil takes place. The cracked vapors are then transferred to a fractionating column through cyclone separator which allows only cracked vapors and catalyst is retained in the reactor itself.



**Fig.5.3** Fluidized (Moving) bed catalytic cracking



After some time, the catalyst gets deactivated due to the deposition of carbon and oil on its surface. The deactivated catalyst is conveyed into a regenerator by hot air blower where the deposited oil is stripped by steam and the deposited carbon is converted into CO<sub>2</sub> using hot air. The CO<sub>2</sub> is allowed to escape using a cyclone separator and the regenerated catalyst is again used for cracking fresh batch of heavy oil.

### Optimum Conditions:

Feed oil	heavy oil
Temperature	550 °C
Pressure	1 – 2 atmosphere
Catalyst	Al <sub>2</sub> O <sub>3</sub> + SiO <sub>2</sub>
Yield	10 <sup>6</sup> gallons per day

The advantage of fluidized cracking process is that high degree of mixing is achieved and consequently, a good contact is established between the catalyst and vapor. The results not only give higher yield but also gasoline of better quality.

### Advantages of catalytic cracking over thermal cracking

- (1) Yield of petrol is higher
- (2) Better quality gasoline is obtained
- (3) No external fuel is necessary for cracking
- (4) Lower pressure (about 1- 2 atmosphere) is needed in catalytic cracking
- (5) The product of cracking contains higher amount of aromatics and hence, it possesses better antiknock characteristics.
- (6) Catalysts are selective in their action and therefore they permit cracking of only high boiling hydrocarbons.

### Reforming of petrol:

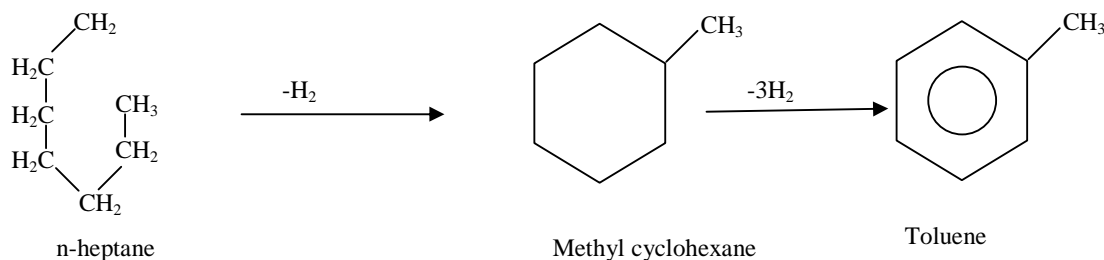
The primary object of reforming is to improve the antiknock characteristics or octane number of gasoline. *“Reforming is a process carried out to improve the octane number of petrol (obtained from fractional distillation) by bringing about modifications in the structure of hydrocarbons.”* It can be carried out either thermally or in presence of a catalyst. The modifications in the structure could be isomerization, dehydrogenation, dehydrocyclization, hydrocracking etc.

The main reactions during catalytic reforming process are:

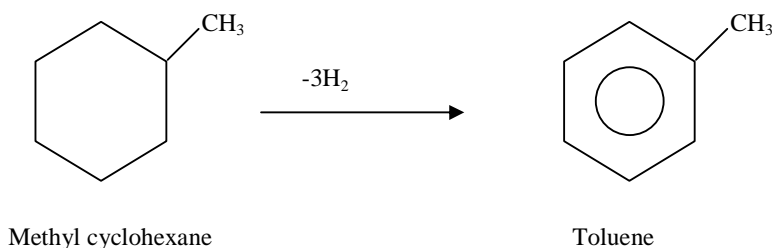
**i) Isomerization:** Straight chain hydrocarbons are converted into branched chain hydrocarbons



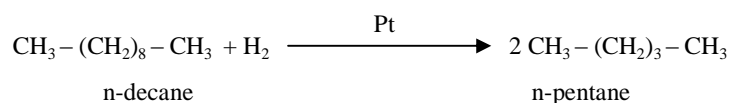
**ii) Dehydrocyclization:** Straight chain compounds are converted into cyclic compounds



**iii) Dehydrogenation:** Cyclic compounds are dehydrogenated to get aromatic compounds.



**iv) Hydrocracking:** Higher alkanes undergo hydrocracking in presence of  $H_2$  and catalyst to produce smaller fragments high octane number



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**Knocking and its mechanism**

In an IC engine, the gasoline vapor – air mixture is drawn into the cylinder. Then, the mixture is compressed by the piston and ignited by a spark in the cylinder. The hydrocarbons in gasoline undergo complete combustion and flame spreads rapidly and smoothly. The energy is released at a uniform rate.

Sometimes, due to the deposition of carbon on the walls of the cylinder the hydrocarbons in gasoline form peroxides. The formation of peroxides is a slow process, i.e. energy is released at a slow rate. The accumulated peroxides decompose suddenly and burst into flames producing pressure waves known as shock waves i.e. energy released at a very fast rate. The shock wave hits the walls of the engine and the piston with a rattling sound.

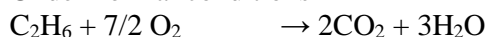
The efficiency and power out put of an internal combustion engine depends on compression ratio. The compression ratio is the ratio of the volume of the cylinder at

the end of suction stroke to the volume ( $V_2$ ) of the cylinder at the end of compression stroke. Since  $V_1 > V_2$ , this ratio is always greater than one. The efficiency of an internal combustion engine increases with increase in compression ratio, which is dependent on the nature of constituents present in the gasoline used.

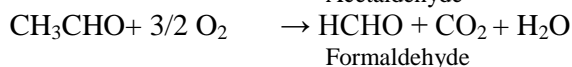
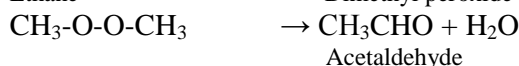
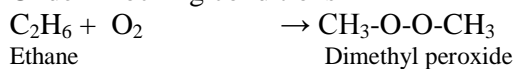
*“Knocking may be defined as the production of a shock wave in an IC engine as a result of an explosive combustion of fuel-air mixture consequently to an increase in the compression ratio, beyond a certain value, leading to a rattling sound.”*

The reactions that take place in an IC engine are given below (taking combustion of ethane as an example);

Under normal conditions



Under knocking conditions



The tendency of the fuel constituents to knock is of the following order

***Straight chain Hydrocarbons > branched Chain Hydrocarbons > alkenes > cycloalkanes > aromatics***

### **Ill effects of knocking:**

- 1) Undesirable noise
- 2) Increase of fuel consumption
- 3) Mechanical damage to engine parts such as spark plug, piston etc.

### **Remedies:**

- 1) Change in I.C. engine design
- 2) Use of optimum compression ratio
- 3) Use of high rating gasoline
- 4) Use of antiknocking agents

### **Prevention of knocking:**

The knocking can be prevented or reduced by using

- (a) Antiknocking agents
- (b) Unleaded petrol

**(a) Antiknocking agents:** Addition of 1-2 cm<sup>3</sup> of tetraethyl lead (TEL), (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Pb to 1 litre of petrol increases the octane number of petrol by 8 to 10 units.

According to most accepted theory, 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 thus, decreasing the chances of any early detonation. However, deposit

of lead oxide is harmful to the engine life. Consequently, in order to help the simultaneous elimination of lead oxide formed from the engine, a small amount of dibromo ethane is also added to petrol. Dibromo ethane converts lead oxide into volatile lead bromide, which escapes with the exhaust gases.

The release of lead compounds pollutes the atmosphere. Catalytic converters are used in IC engines to convert CO to CO<sub>2</sub>. The TEL poisons the catalyst and hence leaded petrol is not advisable in such IC engines.

### (b) Unleaded petrol:

The unleaded petrol is the one which does not contain any lead compound. Octane number of unleaded petrol can be increased by adding certain substances like isopentane, ethyl benzene, isopropyl benzene etc. in place of TEL. In addition to it, compounds like methyl tertiary butyl ether (MTBE) are added to improve the octane number of unleaded petrol. The oxygen of MTBE brings about complete combustion of petrol preventing peroxide formation and hence knocking is prevented. MTBE can be used as antiknocking agent in IC engines with catalytic converter.

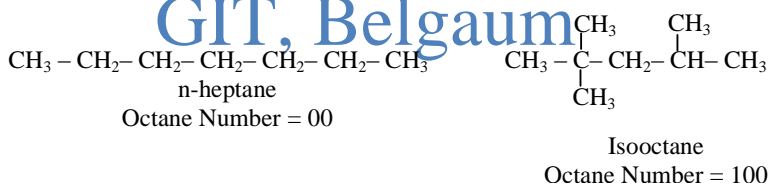
### Octane number

The quality of petrol is determined by an arbitrary scale called octane number. Higher the octane number better is the quality of the petrol.

*“Octane number is the percentage by volume of isooctane present in a mixture of isooctane and n-heptane, which has the same knocking characteristic as the petrol under test”.*

It has been found that n-heptane knocks very badly and hence, it has been arbitrarily assigned an octane number of zero. On the other hand iso-octane produces minimum knocking and has been assigned an octane number of 100.

A series of standard mixtures of isooctane and n-heptane are prepared and the compression ratio of each of these is determined under standard conditions. The compression ratio of the petrol under test is also determined under the same conditions. For example, if the compression ratio of petrol matches with that of 75:25 mixture of isooctane and n-heptane then the octane number of the petrol is 75.



Automobile petrols have octane number ranging from 75 to 95. Aviation petrols have a greater octane number than isooctane, i.e., their octane numbers are greater than 100. In such cases, the octane numbers are computed using the relationship

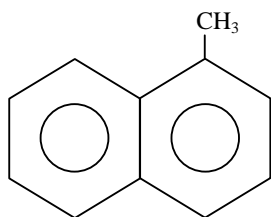
$$\text{Octane number} = \frac{(\text{Power number} - 100)}{3} + 100$$

Where the power number is an arbitrary number proportional to the power being extracted by the engine

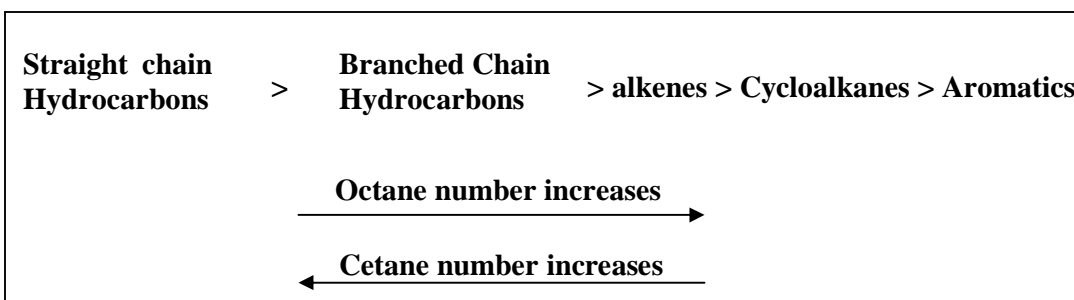
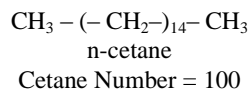
### Cetane number

The quality of diesel is determined by an arbitrary scale called cetane number. Higher the cetane number better is the quality of diesel. “Cetane number is the percentage by volume of *n*-hexadecane present in a mixture of *n*-hexadecane and  $\alpha$ -methyl naphthalene, which has the same knocking characteristic (or ignition lag) as the diesel under test”.

It has been found that  $\alpha$ -methyl naphthalene has long ignition lag and hence, it has been arbitrarily assigned a cetane number of zero. On the other hand *n*-hexadecane has low ignition lag and has been arbitrarily assigned a cetane number of 100.



$\alpha$ -methyl naphthalene  
Cetane number = 00



The good petrol is a bad diesel. Knocking in a petrol engine and in a diesel engine is due to two different reasons. In petrol engine it is due to the sudden spontaneous combustion of last part of the mixture and in diesel engine it is due to the delay in the spontaneous combustion of the first part of the oil. The result is that an oil of high octane number has low cetane number and vice versa. Hence, diesel cannot be used for petrol engines and vice versa.

### POWER ALCOHOL

Power alcohol is a mixture of petrol and ethyl alcohol used in IC engines with varying percentage of ethyl alcohol. The concept of power alcohol for IC engines was first suggested by Henry Ford in 1920. Blends from 10% to 25% of alcohol with petrol are used as fuel in IC engines. Absolute alcohol is used in the preparation of

power alcohol to avoid phase separation. Alcohol is used as an additive but not as a fuel.

#### **Advantages of power alcohol**

- 1) Ethyl alcohol can be synthesized in large quantities from by products of sugar industries and agricultural products. Hence it is cheap and renewable
- 2) Alcohol contains easily oxidisable OH group and contains higher percentage of oxygen than MTBE, which brings about complete combustion of hydrocarbons in petrol
- 3) Its octane number is high and does not release CO during combustion; hence it causes less pollution.
- 4) It is biodegradable
- 5) Power alcohol and pure petrol have same lubrication.
- 6) Alcohol has octane number of 90 while petrol has an octane number of 60-70. Addition of alcohol increases the octane number of petrol.

#### **Disadvantages of power alcohol**

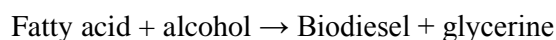
- 1) Alcohol reduces the calorific value of petrol, since its calorific value is 2/3 of that of petrol.
- 2) It is difficult to atomize alcohol as it has considerable surface tension, particularly at low temperatures. Hence, specific arrangements should be made in the carburetor to start the engine.
- 3) Alcohol is easily oxidized to acids. Hence, it may cause corrosion.

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Biodiesel is referred to as the mono alkyl esters of long chain fatty acids derived from renewable lipid sources like vegetable oils or animal fats. Biodiesels can be used in any diesel engine. In pure form biodiesel is readily biodegradable, non-toxic and essentially free from sulfur and aromatics.

#### **Synthesis of Biodiesel**

Biodiesels are synthesized from triglycerides, three fatty esters connected to a glycerine “backbone”. These triglycerides are transesterified when they are mixed with an alcohol in the presence of sodium hydroxide. The reaction produces an ester and glycerine, a valuable by product.



#### **“B” factor**

“B” factor is a labeling system used to state the amount of biodiesel in the mixture of biodiesel and petroleum diesel.

A fuel containing 100% biodiesel is labeled as B100 while

20% biodiesel is labeled as B20,

5% biodiesel is labeled as B5,

2% biodiesel is labeled as B2.

Blends up to 20% biodiesel with 80% petroleum diesel (B2, B5 and B20) can generally be used in unmodified diesel engines. A biodiesel can be used in its pure form (B100) but may require certain engine modifications to avoid maintenance and performance problems.

### **Advantages**

- a. Biodiesels can be used in any diesel engine. Needs no engine modification up to 20% blend (B20)
- b. Good for vehicles as better lubricant and solvent properties – no fuel line or engine deposits
- c. Biodiesels are supposed to be carbon neutral, i.e. the amount of carbon they emit is equal to the carbon extracted from the atmosphere while being produced via photosynthesis.
- d. They are renewable energy sources
- e. Biodiesels have some emission benefits as they produce less CO<sub>2</sub>, no SO<sub>2</sub> and also reduce the emission of CO and soot.

## **Photovoltaic cells**

### **Introduction**

Energy directly obtained from the sun is called solar energy. Solar energy can be a major source of power. Its potential is 178 billion MW which is about 20,000 times the world's demand. But so far it could not be developed on a large scale. Sun's energy can be utilized as thermal and photovoltaics. Solar energy has the greatest potential of all the sources of renewable energy and if only a small amount of this form of energy could be used, it will be one of the most important supplies of energy especially when other sources in the country have depleted.

The rate at which solar energy arrives at the top of the atmosphere is called the solar constant  $I_{sc}$ . This is the amount of energy received in unit time on a unit area perpendicular to the sun's direction at the mean distance of the earth from the sun.

$$I_{sc} = 1.353 \text{ kW m}^{-2}$$

Photovoltaic cell is based on photoelectric effect. This was first discovered by a French physicist Edmond Becquerel 1839. He found that certain materials produce small amount of current when exposed to sunlight. In 1905 Albert Einstein explained photoelectric effect on which photoelectric technology based and for which he won Nobel Prize. Photovoltaic cells provide a clean pollution free and environmental friendly source of electricity. Photovoltaics is the future source of sustainable energy

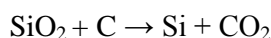
and a considerable amount of money is spent on research and development of photovoltaic cells.

*A photovoltaic cell is basically a P-N junction diode which converts solar energy into electrical energy. It is also called solar energy converter.*

Silicon is a semiconductor material; its band gap is 1.12 eV at 298K. The refractive index of silicon is high. The silicon transmits almost all infra red light. The absorption and transmission properties in the 0.4 to 0.5  $\mu\text{m}$  wavelength spectra are important in the performance of photovoltaic cells.

### **Production of metallurgical grade silicon;**

Metallurgical grade silicon (purity 98. 5%) is prepared by the reaction of high purity silica with coal or coke in an electrical arc furnace using carbon electrodes at 1900 °C.



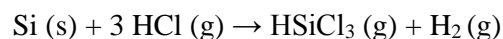
Liquid silicon collected at the bottom of the furnace is drained and then cooled. The crude silicon liquid is treated with sand and lime or limestone to remove Al, Mg and Ca etc. The solidified silicon is crushed into small lumps up 100 mm in jaw crushers.

### **Production of solar grade silicon;**

Semiconductor industry demands high purity silicon with impurity levels in ppb or ppt. This is achieved by the preparation of a volatile silicon hydride and its purification by fractional distillation. This is followed by decomposition of hydride to high purity elemental silicon by chemical vapour deposition.

### **Siemens Process**

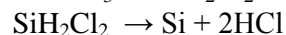
Trichlorosilane is produced by heating metallurgical grade silicon with hydrogen chloride at 350°C.



The trichlorosilane formed is purified through fractional distillation to eliminate heavier and lighter components other than trichlorosilane.

The thermal decomposition of trichlorosilane is carried out by heating on silicon rod at 1100°C in a deposition chamber.

The reactions occurring in the process are;

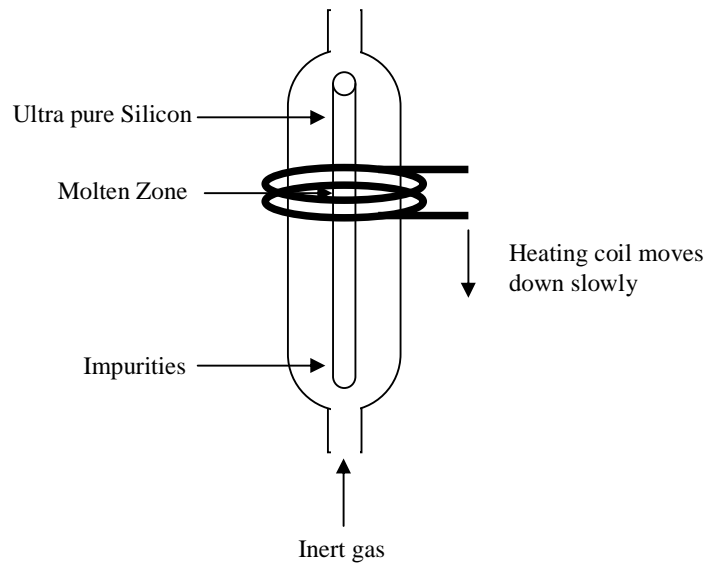


### **Purification of Silicon by zone refining**

Zone refining was developed by Bill Pfann in Bell telephone laboratories as a method to prepare high purity semiconductor materials.



In zone refining, the metallurgical grade silicon rod is first heated to melt at one end and then, the heater is slowly moved down the length of the rod. Most of the impurities tend to remain in the molten region rather than resolidify but silicon cools and resolidifies behind it. When the process is complete most of the impurities in the rod will have been moved into the other end. This end is then cut off and discarded. This process is repeated to get higher purity.



**Fig. 5.4** Zone refining

### **Doping of silicon**

*“The process of adding desirable impurity to a pure semiconductor in a controlled manner is called doping.”*

If the pure silicon is doped with pentavalent impurity like P, As, Sb, Bi etc. then it is called n-type semiconductor.

If the pure silicon is doped with trivalent impurity like In, B, Al, Ga etc. then it is called p-type semiconductor.

There are various techniques of adding impurities to solar grade silicon. The two important techniques of doping of silicon are diffusion technique and ion implantation technique.

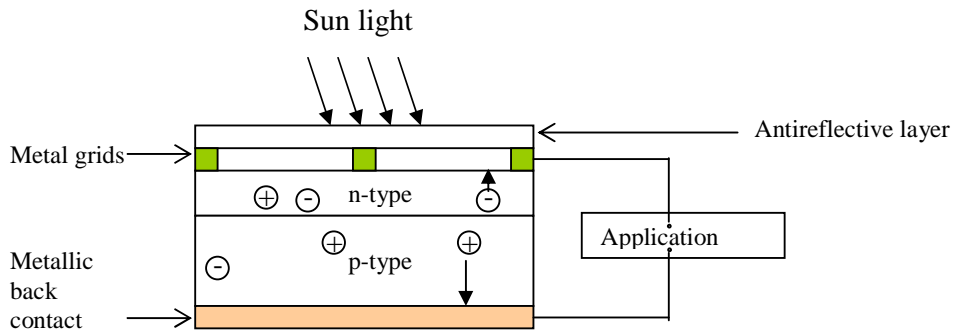
### **Diffusion technique**

In diffusion technique, the silicon wafer is heated to a temperature just below the melting point in a diffusion chamber in an atmosphere of impurity (pentavalent or trivalent). The impurity atoms condense on the surface of the silicon wafer and diffuse into the crystal. The extent of diffusion of impurity can be controlled by varying the temperature and concentration of the impurity.

### **Ion implantation technique of doping of silicon**

In ion implantation technique the silicon is impacted with an ion beam of impurity ions, as a result the implantation of some impurity atoms into the crystal lattice of silicon takes place. The extent of doping can be controlled by the energy of the ion beam.

## Working of Photovoltaic cell



**Fig. 5.4** Photovoltaic cell

Silicon photovoltaic cell is composed of a thin wafer (250 – 300  $\mu\text{m}$ ) consisting of an ultra thin layer of phosphorous doped (n-type) silicon on top of the boron doped (p-type) silicon. Hence, a p-n junction is formed between the two. A metallic grid forms one of the electrical contacts of the diode and allows light to fall on the semiconductor between the grid lines. An antireflective layer ( $\text{TiO}_2$  or  $\text{SiN}$ ) between the grid lines increases the amount of light transmitted to the semiconductor. The cell's other electrical contact is formed by a metallic layer on the back of the solar cell.

When light radiation falls on the p-n junction diode, electron hole pairs are generated by the absorption of the radiation. The electrons are drifted to and collected at the n-type end and the holes are drifted to and collected at the p-type end. A strong electric barrier exists at the depletion region. When these two ends are electrically connected through a conductor there is a flow of current between the two ends through the external circuit. Thus photoelectric current is produced and available for use.

The current out put of a cell depends on its size and efficiency, which is proportional to the intensity of solar radiation striking on the surface of the cell. Photovoltaic cells are connected in series or parallel circuits to produce higher voltages.

### Advantages of photovoltaic cells

- 1) Photovoltaics is considered to be the future sustainable energy system, which unlimited and renewable.
- 2) Photovoltaic cells provide power for space craft and satellites.
- 3) Developments in the field photovoltaic cell will boost the semiconductor industry.
- 4) Photovoltaic energy conversion is highly modular. Power supply to remote areas where the grid extension is economically not feasible.
- 5) Low operating cost.
- 6) No moving parts and no wear and tear
- 7) Quick installation.
- 8) No emissions, no combustion residues for disposal, which does not contribute to global warming.
- 9) Excellent safety record and public acceptance is high.

## Review Questions

- 1) What are chemical fuels? Give complete classification of chemical fuels with examples.
- 2) Define i) Calorific value ii) Gross calorific value iii) Net calorific value
- 3) Describe how the calorific value of a solid fuel or liquid fuel is determined using a bomb calorimeter.
- 4) What is meant by cracking? Explain fluidized bed catalytic cracking with a neat diagram.
- 5) What are the advantages of catalytic cracking over thermal cracking?
- 6) What is meant by reforming explain the principal reactions occurring during reforming process?
- 7) What is meant by knocking in IC engine? Explain the mechanism of knocking taking combustion of ethane as an example.
- 8) What is knocking in IC engine? What are its ill effects? How knocking can be prevented?
- 9) Explain i) Octane number ii) Cetane number
- 10) Give an account of i) antiknocking agents ii) Unleaded petrol
- 11) What is power alcohol? What are the advantages and disadvantages of blending alcohol with petrol?
- 12) What is a biodiesel? Explain the synthesis of biodiesel by transesterification method and mention its advantages.
- 13) What are catalytic converters? Explain the principle and working of catalytic converter with neat diagram.
- 14) What are photovoltaic cells? Explain the construction and working of photovoltaic cell.
- 15) Explain the production of solar grade silicon by chemical vapour deposition.
- 16) Explain the method of purification of silicon by zone refining.
- 17) What do you mean by doping of silicon? Explain doping of silicon by diffusion technique.
- 18) What are the various applications of solar cells?
- 19) Calculate the GCV and NCV of a coal sample from the following data:  
Weight of coal sample taken =  $8.5 \times 10^{-4}$  kg  
Weight of water = 3.5 kg  
Water equivalent of calorimeter = 0.5 kg  
Initial temperature of water =  $25^{\circ}\text{C}$   
Final temperature of water =  $27.5^{\circ}\text{C}$   
Specific heat of water =  $4.187 \text{ kJ kg}^{-1} \text{ K}^{-1}$   
Latent heat of steam =  $587 \times 4.187 \text{ kJ kg}^{-1}$   
% of hydrogen in the coal sample = 2.5%  
(Ans: GCV = 49258.82 kJ kg<sup>-1</sup>, NCV = 48706.44 kJ kg<sup>-1</sup>) (VTU July 2004)
- 20) 0.935 g of fuel underwent complete combustion in excess of oxygen, the increase in temperature of water in a calorimeter containing 1365 g of water was  $2.4^{\circ}\text{C}$ . Calculate the GCV of the fuel, if the water equivalent of calorimeter is 135g.  
(Ans: GCV = 16121.06 kJ kg<sup>-1</sup>)
- 21) On burning 0.96 g of solid fuel in a bomb calorimeter the temperature of 3500 g of water increased by  $2.7^{\circ}\text{C}$ . Water equivalent of calorimeter and latent heat of steam are 385 g and 587 cal g<sup>-1</sup> respectively. If the fuel contains 5% of hydrogen, calculate its GCV and NCV.  
(Ans: GCV = 45749.5 kJ kg<sup>-1</sup>, NCV = 44643.5 kJ kg<sup>-1</sup>) (VTU Jan 2007)

### Objective type questions

- 1) A good fuel should possess  
a) low calorific value   b) high ignition temperature  
**c) high calorific value**   d) high ash content
- 2) For good performance the hydrocarbon molecules in diesel fuel should be  
a) branch-chained   **b) straight chained**   c) side chained   d) aromatic
- 3) The quality of the petrol is judged by  
**a) octane rating**   b) cetane rating   c) % of carbon   d) length of carbon chain
- 4) Which of the following is a secondary fuel  
a) wood   b) lignite   c) coal   **d) charcoal**
- 5) If the percentage of hydrogen in a fuel is high, its net calorific value is  
a) high   **b) low**   c) constant   d) cannot be predicted
- 6) Which of the following possesses zero octane number?  
a) Isooctane   b)  $\alpha$ -methyl naphthalene   **c) n-heptane**   d) Cyclohexane
- 7) Bomb calorimeter is used for the determination of calorific value of  
a) liquid fuel   b) solid fuel   c) gaseous fuel   **d) both a) and b)**
- 8) Gas with least calorific value  
a) coal gas   b) water gas   c) natural gas   **d) producer gas**
- 9) Gas with highest calorific value  
a) coal gas   b) water gas   **c) natural gas**   d) producer gas
- 10) Bomb calorimeter is used to determine  
a) GCV at constant pressure   **b) GCV at constant volume**  
c) NCV at constant volume   d) NCV at constant pressure
- 11) A process carried out to improve the octane number of petrol by bringing about modifications in the structure of hydrocarbon is called  
**a) reforming**   b) cracking   c) pyrolysis   d) combustion
- 12) A process in which long chain hydrocarbons of high molecular weight and high boiling point are broken down to smaller fragments of lower boiling point and lower molecular weight is called  
**a) cracking**   b) reforming   c) pyrolysis   d) knocking
- 13) Octane number of isooctane is  
**a) 50**   b) zero   **c) 100**   d) 24
- 14) Which of the following possesses zero cetane number?  
a) Isooctane   **b)  $\alpha$ -methyl naphthalene**   c) n-heptane   d) Cyclohexane

15) Percentage of isooctane in a mixture of n-heptane and isooctane which matches the fuel in knocking characteristics is called

- a) cetane number      **b) octane number**      c) Ignition point      d) knocking

16) Knocking in an IC engine is produced as a result of \_ \_ \_ \_ combustion of fuel-air mixture

- a) Slow      **b) explosive**      c) moderate      d) none of these

17) Knocking in IC engine is due to the rapid decomposition of

- a) Aldehydes      b) Ketones      **c) peroxides**      d) none of these

18) Tetra ethyl lead is added to petrol

- a) to enhance octane number**      b) to enhance cetane number  
c) to reduce octane number      d) to reduce cetane number

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