Module 3: Fuels & Solar Energy

3.1 Introduction

Chemical fuel: are naturally occurring or artificially made carbonaceous combustible substance, which on combustion liberates a large amount of energy.

3.1.1 *Classification:* Fuels are classified as primary and secondary fuels.

3.1.1.1 Primary fuels: Fuels that occur in nature and are directly used without processing is called primary fuels. They are raw fuels. Examples are wood, coal, petroleum, natural gas, animal dung, etc.

3.1.1.2 Secondary fuels: Fuels that are obtained by chemical processing and prepared from raw or primary fuels are called secondary fuels. Examples are charcoal, coke, coal gas, gobar gas, water gas. Based on the physical states both primary and secondary fuels are sub classified as solid, liquid and gas.

	Primary	**Secondary**
Solid	Coal, Wood, Animal dung	Charcoal, Coke.
Liquid	Crude petroleum oil.	Petrol, Diesel, kerosene.
Gas	Natural gas.	Coal gas, gobar gas, water

		gas.

3.2 *Calorific value* of a fuel is defined as "***The amount of heat energy liberated when a unit quantity (volume or mass) of the fuel is burnt completely in presence of air or oxygen under standard condition***."

The S.I unit of calorific values is

Solid and Liquid fuel = Jg^{-1} (J/g) or $kJkg^{-1}$ (kJ/kg)

Gaseous fuel = Jcm^{-3} (J/cm^3) or kJm^{-3} (kJ/m^3)

Calorific value of fuel is measured either as gross calorific value or net calorific value.

3.2.1 Gross calorific value (GCV, Higher calorific value HCV): "***The amount of heat energy liberated when the unit quantity of fuel is burnt in an isolated container in presence of air / oxygen and the products are cooled (condensed) to room temperature.***"

UsuallyCO_2 and H_2O is the major products of a fuel thus GCV is,

GCV = NCV + heat associated with steam

3.2.2 Net calorific value (NCV Low calorific value LCV): ***"The amount of heat energy liberated when the unit quantity of fuel is burnt in presence of air / oxygen and the products are allowed to escape."***

NCV = GCV - heat associated with steam.

3.2.2.1Calculation of heat associated with steam

$H_2 + ½\, O_2 \longrightarrow H_2O$

2 kg of hydrogen produces 18 kg of water, therefore

$$\text{x kg of hydrogen produces} = \frac{18x}{2}\ \text{kg of water}$$

Water produced by 100 kg of fuel $= \frac{18}{2} \times \frac{x}{100} = 0.09\,x$ kg of water

Heat associated with steam = weight of water produced X latent heat of steam

(Latent heat of steam = 587 X 4.2kJ/kg)

$$\boxed{\text{LHV} = 0.09\,x \times 587 \times 4.2 \text{ kJ/kg}}$$

3.3 Determination of calorific value of a solid or liquid fuel using bomb calorimeter

A bomb calorimeter is a type of constant-volume calorimeter used in measuring the heat of combustion (calorific value) of a particular substance. Using electrical energy the fuel is burnt in presence of excess of oxygen which heat up the surrounding air. This heated air while escaping through the tube heat up the water outside the tube. The change in temperature of the water is measured using sensitive thermometers. Using the change in temperature the calorific value of the fuel is calculated.

Apparatus

The bomb calorimeter is constructed as shown in figure 3.1. It consists of two units.

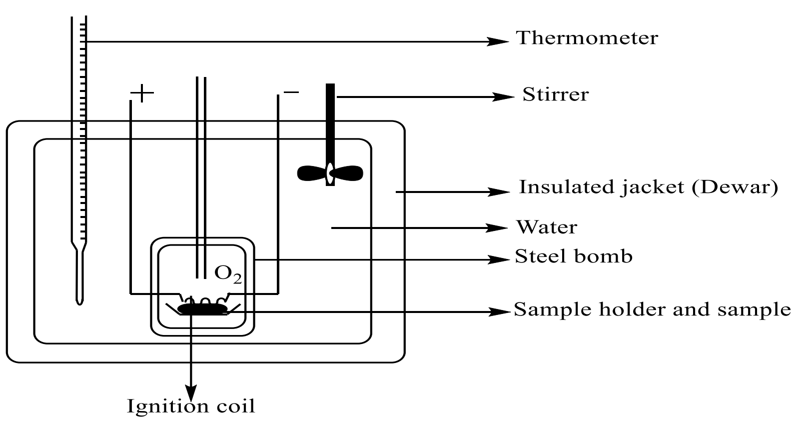


Figure 3.1 Schematic diagram of bomb calorimeter

Steel bomb

- Steel cylinder (steel bomb) which can withstand high pressure.
- A gas inlet tube to fill oxygen in steel bomb at 25 atm pressure.
- A platinum sample holder.
- An electric coil to ignite the fuel.

Dewar flask: This complete unit of steel bomb is placed inside a dewar (Insulated brass chamber) filled with water. A sensitive thermometer and a stirrer are provided to the dewar.

Working: A known quantity of fuel sample is taken in the sample holder and is placed in the steel bomb. The bomb is charged with oxygen at 25 atm pressure. Initial temperature of the water is noted. The sample is ignited using electric coil, the fuel starts burning liberating the heat which is absorbed by water in the calorimeter. The final temperature is noted.

Calculation of GCV

m = Mass of the fuel
W_1 = Mass of water
W_2 = Water equivalent mass of calorimeter and other accessories.
T_1 = Initial temperature
T_2 = Final temperature
S = specific heat of water
Heat loss by m kg of a fuel = heat gained by calorimeter + water

Heat associated with the fuel = mass X sp. Heat X change in temperature

$$= (W_1 - W_2) \text{ X } 4.187 \text{ X } (T_2 - T_1)$$

$$\boxed{GCV = \frac{(W_1 + W_2) \text{ X } 4.187 \text{ X } (T_2 - T_1)}{m} \text{ (kJ/kg)}}$$

Crude oil: Primary distillation yields about 20 – 30 % by quantity of petrol which is not sufficient in market. Thus some of the fractions are physiochemically processed to yield more petrol. Two important chemical processing of petroleum crude oil is by cracking and reformation.

3.4 Knocking

Explosive combustion of air-fuel mixture due to the variation in compression ratio produces shock waves which hit the cylinder wall and piston of engine, creating rattling sound known as knocking.

3.4.1 Mechanism, ill effects and prevention of Knocking in petrol engine

In petrol engine air and petrol are mixed together and then compressed, whereas in diesel engine air is compressed and then the fuel is injected into the compressed air. The ratio of the gaseous volume in the cylinder at the end of the suction-stroke to the volume at the end of compression ratio.

In an engine under normal compression ratio the initiation of the combustion of petrol-air mixture undergoes under normal conditions and rate of flame propagates at 20-25 ms^{-1}. However, beyond a particular compression ratio, premature combustion occurs due to which petrol-air mixture suddenly bursts into flames and propagates at 2500 ms^{-1}. This process is accompanied by a sharp knock in the engine due to explosive combustion producing a shock wave which loses its energy by hitting the cylinder wall and piston. As a result, rattling sound is heard which is referred to as the knocking.

Under normal compression ratio

$$C_2H_6 + 7/_2\,O_2 \longrightarrow 2CO_2 + 3H_2O$$

Ubnormal Combustion leads chain reaction

$$C_2H_6 + O_2 \longrightarrow H_3C{-}O{-}O{-}CH_3$$

$$H_3C{-}O{-}O{-}CH_3 \longrightarrow CH_3CHO + H_2O$$

$$CH_3CHO + 3/_2\,O_2 \longrightarrow HCHO + CO_2 + H_2O$$

$$HCHO + O_2 \longrightarrow CO_2 + H_2O$$

Adverse effect	Remedial measures
It produces undesirable rattling noise.	A suitable change in engine design.
It increases the fuel consumption.	By using high rating gasoline.
It results in decreased power output.	By using critical compression ratio.
It causes mechanical damage due to overheating, to engine parts such as spark-plug, piston and engine walls.	By using anti-knocking agents.
The driving becomes unpleasant.	

3.5 Power alcohol:

Power alcohol is gasoline blends containing ethanol which can be used as a fuel in internal combustion engines. Blend containing up to 25% of alcohol with petrol are used. The main objective of the power alcohol was to reduce oil imports and provide an alternative to non-renewable energy source, gasoline.

The importance of power alcohol as fuel is:

1. Alcohol has an octane number of 90 while petrol has octane number of 60-70. Addition of alcohol to petrol amplifies the octane number. Hence power alcohol possesses better anti-knock properties.

2. Because of the higher octane number, alcohol-blended petrol can be used in engines with higher compression ratio. This compensates for the lower heating value of alcohol in the blend.

3. There are no starting difficulties with alcohol-petrol blend.

4. Lubrication in case of alcohol-petrol blend and pure petrol is the same.

5. Ethanol is biodegradable.

3.6 Unleaded Petrol

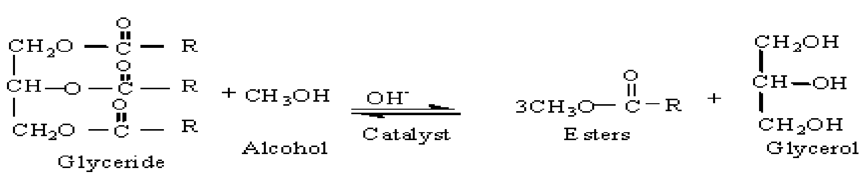
The use of TEL, TML etc, combustion of leaded petrol leads to formation of PbO, which deposits on the inner wall of cylinder and jams the piston. Also leads to exhaust poisonous gases. Hence alternatice method of avoiding knocking and increasing octane number is by adding high octane compounds like isopentane, isooctane, ethyl benzene, isopropyl benzene, methyl tertiary butyl ether (MTBE). MTBE is preferred because it contains oxygen in the form of ether group and supplies oxygen for the combustion of petrol in internal combustion engines, thereby reducing unleaded petrol.

The importance of unleaded petrol as fuel is:

- Eliminates the pollution level of lead in atmosphere.
- This permits the attachment of catalytic converters to the exhaust pipe in automobiles.

3.7 Biodiesel

Biodiesel is commonly produced by the transesterification of the vegetable oil or animal fat feedstock and is meant to be used in standard diesel engines. Biodiesel can be used alone, or can be blended with diesel.



Advantages:

i. Biodiesel can also be used as a low carbon alternative to heating oil.
ii. Biodiesel has better lubricating properties.
iii. Biodiesel has higher cetane ratings than lower sulfur diesel fuels.

iv. Biodiesel addition reduces fuel system wear and increases the life of the fuel injection equipment

v. Biodiesel has virtually no sulfur content and it is often used as an additive to Ultra-Low Sulfur Diesel (ULSD) fuel to aid with lubrication.

Fuel Cells

3.8 Introduction

"Fuel cell is a galvanic cell in which chemical energy of a fuel is directly converted into electrical energy by means of redox reactions involved with oxidants".

$$Fuel + Oxidant \rightarrow Oxidized\ product + Reduced\ Product$$

3.9 Difference between battery and fuel cell:

The fuel cell differs from a battery in the following aspects.	
Fuel Cell	**Batteries**
Reactants are fed from outside	Reactants are kept inside
Fuel cells does not store chemical energy, it is an energy conversion device.	Batteries are Energy storage device
Electrical energy is continuous process till the reactants are supplied constantly.	Electrical energy is generated until reaction is complete.
The products are constantly removed from the cell.	The products are not removed from the cell.

3.10 Advantages & Disadvantages of fuel cell:

Advantages	Disadvantages
High efficiency conversion and energy density.	High initial cost (catalyst, membranes etc).
Low pollution level, no noxious exhaust gases formed.	Large weight and volume of gas fuel storage systems.
Low maintenance, exchangeable parts.	High price of clean hydrogen.

3.11 Construction working and applications of Methanol-Oxygen Fuel cell:

Cell Representation: CH_3OH | Pt | H^+ | Ag | O_2

It is an example of a liquid fuel cell. Construction of fuel cell is shown in figure 1.13. Because the storage and safe handling of hydrogen gas is troublesome, methanol is used instead of hydrogen gas as a reactant. Platinized (catalyst) porous carbon acts as anode. Hollow porous carbon tube impregnated with mixed oxides of Ag, Co and Al (catalyst) acts as cathode. The oxidant is the oxygen or air. Electrolyte is 1M sulphuric acid.

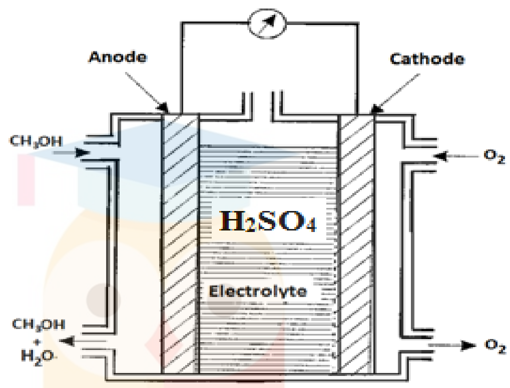


Figure 1.13 Schematic diagram of Fuel cell

- This catalyst can draw hydrogen atoms from liquid methanol.
- Operate in the range from 60°C to 130°C, the emf of the cell is 1.2V.

Anode	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$
Cathode	$3/2 O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$
Overall	$CH_3OH + 3/2 O_2 \rightarrow 2H_2O + CO_2$

Applications:

- H_2-O_2 fuel cells used as the primary source of electrical energy in space craft.

It finds military applications.

3.11 Construction working and applications of Solid oxide (SOFc) Fuel cell:

Cell Representation: H_2 | Co | ZrO_2 | $LaMnO_3$ | O_2

It is an example of a solid oxide fuel cell. Construction of fuel cell is shown in figure 1.13 Anode is made up of porous electrode coated with Co and ZrO_2, cathode contains $LaMnO_3$

doped with strontium. A non-porous solid oxide Zirconia (ZrO_2) is used as an electrolyte doped with about 10mol% of yttria (Y_2O_3), solid fuel helps in migrating the O^{2-} and H_2 or CO is used as a fuel. The cells operate at 650 to 1000^{0}C.

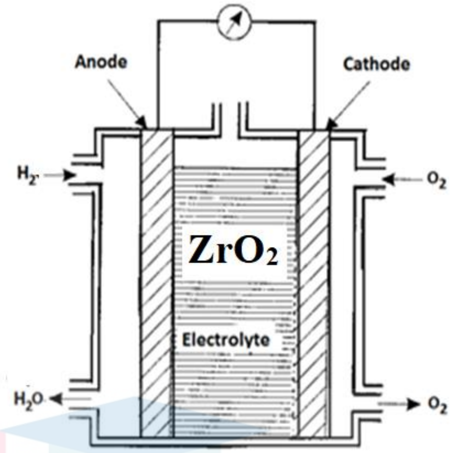


Figure 1.13 Schematic diagram of Fuel cell

Anode	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$
Cathode	$1/2O_2 + 2e^{--} \rightarrow O^{2-}$
Overall	$H_2 + 1/2O_2 \rightarrow H_2O$

Applications:

- SOFCs are used in situations where large amount of heat is required.

Solar Energy

3.13.1 Introduction

The radiations reaching earth from the sun and converting them in to different useful forms of energy is called solar energy. The solar energy can be utilized in two ways,

Direct solar power: Conversion of solar energy directly into electrical energy. Eg., Photo voltaic cell

Indirect solar power: Converting solar energy to chemical energy and later using it. Eg., Photosynthesis, photo degradation of water to hydrogen gas which is used as fuel.

3.14.2 *Photovoltaic cell:* These are the semiconductor device, which convert light energy directly to electrical energy.

The most common material used for solar cells is crystalline silicon, which is the second member in the group IV A in the periodic table. It never occurs free in the nature, but occurs as oxides and silicates. Silicon is the second abundant element found in world.

19 Construction and working of photovoltaic cell

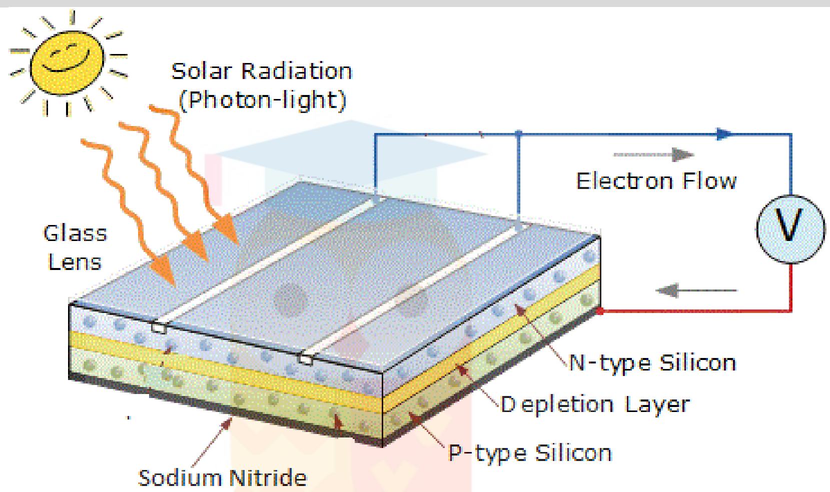


Figure 3.6 Schematic diagram of construction of PVC

PV cells mainly consists of a p-n junction diode made up of Si semiconductor as shown in fig 3.6. It is constructed by two electrical contacts, one is a metallic grid over n-type and second layer of sodium nitride or silver metal at back of the p-type semiconductor. An antireflective layer (silver nitride) or TiO_2 is coated between the metal grids to prevent reflection of solar light.

Working: when sunlight with (photon of energy E=hv) required energy falls on p-n junction, electrons are ejected from electron hole pair in the p-n junction. The ejected electrons move to n-type since the movement in n- type is one way, these ejected electrons must flow through external circuit to combine with holes. These movement of electrons from n side to p side generates electric current.

Electrical energy is directly proportional to area of cell exposed to light radiation and intensity.

3.15 Production of solar grade silicon:

3.16.1 Reduction: Silica SiO_2 is the usual source of silicon. This silica in the form of quartz along with coke is melted in an electric furnace. Silica gets reduced to silicon which is almost 98.5% pure.

$$SiO_2 + C \longrightarrow Si + CO_2$$

3.16.2 Refining: Molten silicon contains impurities such as Mg, Al, Ca (Consider it as M) and etc. This molten silicon is treated with oxygen. Silicon gets converted to silica and the impurities forms silicate slag which will be mechanically removed. The obtained pure silica is of metallurgical grade.

$$\left.\begin{array}{l} Si + O_2 \longrightarrow SiO_2 \\ \qquad\qquad\qquad + \\ 2M + O_2 \longrightarrow MO \end{array}\right\} \longrightarrow \underset{\text{Metal silicate slag}}{MSiO_3}$$

3.16.3 Hydrogenation

The metallurgical grade silica is treated with dry HCl gas at moderate temperature (300 ^oC). This yields a mixture of tri and tetra chlorosilane. The mixture obtained is fractionally distilled and the tetrachlorosilane is recycled to hydrogenation process to obtain trichlorosilane.

$$SiO_2 + HCl \longrightarrow \underset{\text{Trichloro silane}}{HSiCl_3} + \underset{\text{Tetrachloro silane}}{SiCl_4}$$

Trichlorosilane so obtained is passed through columns containing ion exchange resins of quarternary ammonium salts, which acts as catalysts. Trichlorosilane gets converted to dichlorosilane, the process is repeated until silane is obtained

$$HSiCl_3 \xrightarrow[\text{ammonium beds}]{\text{Quarternary}} \underset{\text{Dichloro silane}}{H_2SiCl_2} \xrightarrow[\text{ammonium beds}]{\text{Quarternary}} \underset{\text{Monochloro silane}}{H_3SiCl} \xrightarrow[\text{ammonium beds}]{\text{Quarternary}} \underset{\text{Silane}}{H_4Si}$$

3.16.4 Dehydrogenation and polymerisation

The obtained silane is passed through the beads of pure hot silicon, silane undergoes dehydrogenation giving polymerized silicon which is the semiconductor grade silicon.

$$H_4Si \xrightarrow{\text{Pure Silicon Beads}} \text{Polymeric Silicon}$$

3.16 Advantages and disadvantages of PV Cells

Advantages	Disadvantages
Environmentally friendly energy	High initial cost.
Long term energy	Seasonal energy
Low maintenance.	It is not compact

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