MODULE-3 ENERGY SYSTEMS

Chemical fuels: -

Chemical fuel is a combustible substance containing carbon as the main constituent, which on complete burning produces a large amount of heat which can be used for domestic & industrial purposes.

Calorific Value: -

It is defined as the amount of heat liberated when unit weight (or unit volume in the case of a gaseous fuel) of a fuel is completely burnt in excess of air or oxygen

Gross (Higher) Calorific Value: (GCV)

It is defined as the amount of heat released when unit quantity (unit mass of a solid or liquid fuel or unit volume of a gaseous fuel) of a fuel is burnt completely in air and the combustion products are cooled to room temperature.

Carbon and hydrogen present in fuels are converted into carbon dioxide and steam respectively on combination. On cooling the combination products, steam gets condensed to water and liberate its latent heat. The measured gross calorific value includes the latent heat of steam. Therefore it is always higher than the net calorific value.

Net (Lower) Calorific value: (NCV)

Definition: It is defined as the amount of heat liberated when unit mass of a solid or liquid fuels or unit volume of a gaseous fuel is burnt in excess of oxygen & the products formed are allowed to escape without cooling.

NCV = GCV **–** Latent heat of steam formed (by 1kg of solid or 1m^3 of gaseous fuel)

NC**V =** GCV **–** (mass of hydrogen x 9 x latent heat of steam)

Because one part of hydrogen produces 9 parts of H_2O

The latent heat of steam is 2456 kJ/kg or 4.2 x 587 kJ/kg

SI unit of calorific value: -

The calorific value is normally expressed in calorie per gram (cal/g) in (g) units. It is also expressed in joules per kg (J/ kg) for solid fuels and Joules per cubic meter (J/ m^3) for gaseous fuels in SI units at one atmospheric pressure.

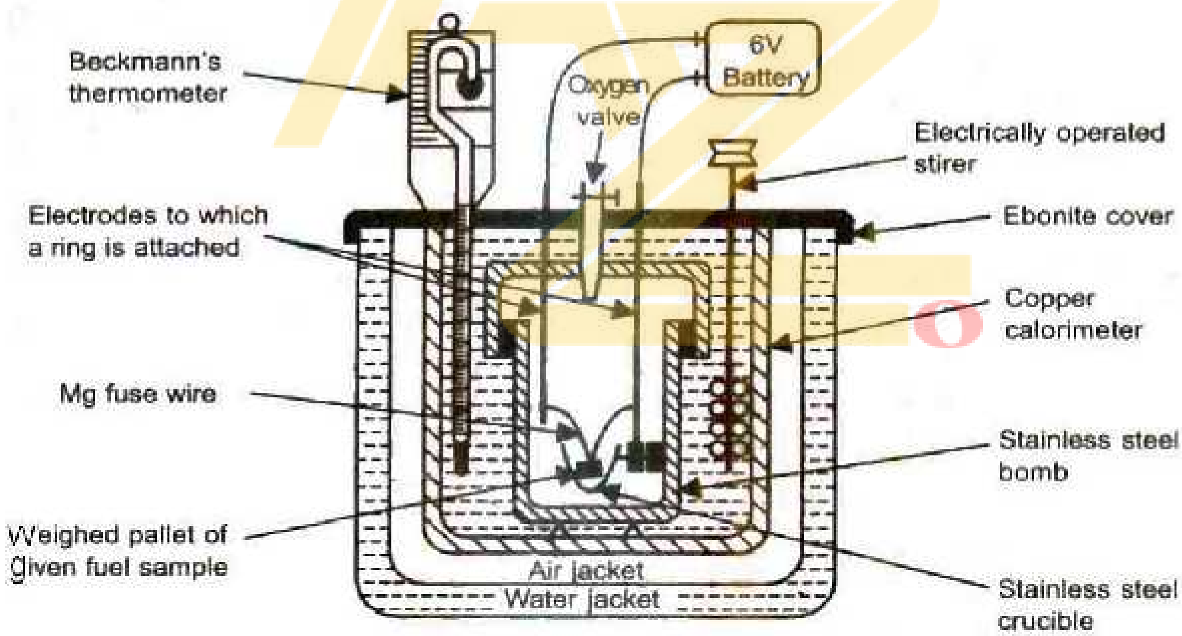
Determination of calorific value of a solid / liquid fuel using Bomb calorimeter: -

Principle: - A known weight of the sample is burnt completely in excess of oxygen. The liberated heat is absorbed by surrounding water and calorimeter. Thus the heat liberated during the combustion of fuel is equal to the heat absorbed by water and copper calorimeter. The higher calorific value of the fuel is calculated from the data.

Construction: - The Bomb calorimeter consists of a cylindrical airtight stainless steel bomb, in which a known weight of fuel (solid or liquid) is taken in a small stainless steel crucible. The two electrodes connected with a magnesium fuse wire is introduced in the bomb for the initiation of combustion of fuel. Also there is an oxygen inlet valve.

The bomb is now immersed in a copper calorimeter containing a weighted mass of water. The copper calorimeter is equipped with a mechanical stirrer for dissipation of heat & a thermometer to read accurately the temperature rise.

The colorimeter is surrounded by an insulated air jacket to minimize heat loss. Externally it is surrounded by a water jacket



Bomb calorimeter

Working: - The water is kept in constant agitation by the mechanical stirrer. The initial temperature of the water is carefully measured. The fused magnesium wire is placed in the fuel. Then bomb is filled with oxygen. The fuel is ignited by connecting the two electrodes to a source of electric current. As the sample burns in the bomb, heat is liberated & is absorbed by the surrounding water & the copper calorimeter. The temperature of water gradually increases; the water in the calorimeter is stirred continuously during the combustion. When the temperature attains the maximum value, (complete combustion) the maximum temperature is noted. The water equivalent of the calorimeter is determined by burning a fuel of known calorific value.From the data obtained in the experiment calorific value is calculated.

Calculations: -

Mass of fuel **= m kg**

Initial temperature of water = $\mathbf{t_1\ {}^0C}$

Maximum temperature of water = $\mathbf{t_2\ {}^0C}$

Rise in temperature of water = $\mathbf{(t_2 - t_1)\ {}^0C} = \mathbf{\Delta t\ {}^0C}$

Mass of water in the calorimeter = $\mathbf{W_1}$ **kg**

Water equivalent of calorimeter = $\mathbf{W_2}$ **kg**

If Q is the gross (total) calorific value of the fuel,

Then heat lost by 'm' g of fuel = Heat gained by water + water equivalent of Cu Calorimeter

$= (W_1+W_2)\ (t_2-t_1)$ cal

The calorific value Q is calculated from the equation

$$Q = \frac{s\,(W1 + W2)\,\Delta t}{m} \quad kJ/kg$$

Where s = 4.184 kJ/kg/^{0}C

Net calorific value: -

Net (lower) calorific value of fuel = GCV – latent heat of water formed

$= GCV - (0.09H \times 587 \times 4.184\ \ kJ/kg)$

Gasoline Knocking:

The efficiency of power production in spark ignited IC engines is related to the compression ratio (CR).

$$\text{Compression Ratio} = \frac{V_1}{V_2}$$

Where V_1 = Cylinder volume (V_1) at the bottom of its stroke (suction)

V_2 = Cylinder volume (V_2) when the piston is at the top of its stroke.(Compression)

"Knocking is the explosive combustion of petrol-air mixture beyond a certain compression ratio, which produces shock waves in IC engine, which hit the walls of the cylinder and piston producing a rattling sound." This is due to the presence of certain constituents in petrol.

Adverse effects of Knocking: -

1. It produces undesirable rattling noise.
2. It increases the fuel consumption.
3. It results in decreased power output.
4. It causes mechanical damage due to overheating to engine parts such as Spark plug, piston and engine walls & reduces the life of the engine.
5. The driving becomes rather unpleasant.

Mechanism of Knocking: -

Under normal conditions there is a slow oxidation of the fuel during which oxygen combines with a few hydrocarbons molecules and activates them by forming peroxides. The activated molecules combine with other hydrocarbon molecules and a chain reaction is set up resulting in smooth combustion. Knocking occurs if the chain reaction proceeds at too fast rate. The unstable peroxides formed decompose explosively giving rise to pressure waves, which knock against the engine walls. The normal and explosive combustion of a fuel (e.g. C_2H_6) may be represented as follows.

$$C_2H_{6\,(g)} + \frac{7}{2} O_{2\,(g)} \longrightarrow 2CO_{2\,(g)} + 3H_2O_{(g)}. \quad \text{(Normal combustion)}$$

$$CH_3-CH_3 + O_2 \longrightarrow CH_3-O-O-CH_3$$

Ethane peroxide.

$$CH_3-O-O-CH_3 \longrightarrow CH_3CHO + H_2O$$

$$CH_3CHO + 3/2\,O_2 \longrightarrow HCHO + CO_2 + H_2O$$

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

Explosive combustion.

Unleaded petrol: -

Since lead compounds are poisonous the use of 'leaded petrol' containing TEL etc is gradually phased out since lead compounds escaping from the exhaust of the engine, pollute the atmosphere. These lead compounds in the air cause several serious health problems.

"Petrol which doesn't contain antiknocking agents such as TEL & other lead compounds is called "Unleaded Petrol".

Mixing of TEL with gasoline brought advantages together with disadvantages. In order to overcome the harmful effects of TEL, it is slowly being phased out from gasoline; the gasoline (petrol) free from lead is called "Unleaded petrol".

In Unleaded petrol the octane number is raised by increasing the quantity of branched chain alkanes, alkenes, & aromatics, since these compounds have high octane number.

Unleaded petrol rating can be enhanced by the addition of certain compounds in place of TEL. Such as, methyl tertiary butyl ether (MTBE), methanol, ethanol etc. MTBE being ether, supplies oxygen for the combustion of petrol in internal combustion engines.

One of the advantages of unleaded petrol is that it allows the use of catalytic converter attached to the exhaust in automobiles. Leaded petrol cannot be used in automobiles equipped with catalytic converter as the lead poisons the catalyst.

Power alcohol: -

When ethyl alcohol is mixed as an additive to motor fuels to act as a fuel for internal combustion engines, it is called power alcohol. Blends containing up to 25% of alcohol with petrol are used.

Blending requires benzene as blending agents, since industrial alcohol contains 95% of alcohol & 5% water. Without the use of blending agent, industrial alcohol does not mix with petrol.

Manufacture of power alcohol: -

Power alcohol (ethyl alcohol) is synthesized from molasses, starches, hydrocarbons & carbohydrates. Molasses is the mother liquor left after the crystallization of sugar from concentrated sugar cane juice. It contains 50-55% total sugar, of which 35-40% is cane sugar or sucrose. Molasses is diluted with water, to bring down the concentration of sugar to 10-12%. pH is kept between 4 &5 to favor the function of enzymes, by using ammonium sulphate & H_2SO_4. Yeast is added to the mixture, which contains enzymes invertase & zymase responsible for fermentation.

$$C_{12}H_{22}O_{11} \longrightarrow \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose or fructose}}{C_6H_{12}O_6} \longrightarrow 2C_2H_5OH + 2CO_2$$

After fermentation for 40-60 hours, it is distilled to get ethyl alcohol which is mixed with water. It contains only about 20% alcohol, which on fractional distillation yields rectified spirit (85%). Repeated distillation & condensation can raise the alcohol content to 97.6%. The concentration of alcohol cannot be increased by distillation beyond 97.6% because it forms a constant boiling mixture has a lower boiling point than alcohol. For internal combustion engine, 100% absolute alcohol should be prepared. Absolute alcohol is prepared by distilling with benzene. Power alcohol (absolute alcohol) may also be prepared by distilling alcohol in the presence of dehydrating agent like lime.

Advantages of alcohol – blended petrol: -

1) Gasoline is produced from fossil fuel, petroleum: whose deposits are fast depleting. Alcohol blended with petrol cuts down the demand for petrol in countries which have no oil deposits of their own.
2) Alcohol is a renewable source of energy since it can be prepared from molasses & other carbohydrate sources.
3) Alcohol has Octane number 90, while petrol has octane number of 60-70. Addition of power alcohol to petrol increases the octane number. Hence alcohol blended petrol possesses better anti-knock properties.
4) There is no starting difficulty with alcohol-petrol blend.
5) Ethanol is biodegradable.

Disadvantages of alcohol – blended petrol: -

1) Alcohol lowers the calorific value of petrol.
2) Alcohol is easily oxidized to acids. Hence alcohol may cause corrosion.
3) Alcohol absorbs moisture and as a result separation of alcohol and petrol layers takes place especially at low temperature. To avoid this, blending agents such as benzene or toluene are used.

Biodiesel:

Biodiesel is a mixture of monoalkyl esters of long chain fatty acids. It is obtained from the renewable sources such as vegetable oils like **soyabeen oil, palm oil, peanut oil, sunflower oil, jathropa oil** and which are essentially triglycerides.

Biodiesel is commonly produced by the trans-esterification of the vegetable oil with virtually any alcohol in presence of catalysts like KOH or H_2SO_4. The most commonly used alcohol is methanol to produce methyl esters (commonly referred to as Fatty Acid Methyl Ester-FAME) as it is the cheapest alcohol available. Ethanol can be used to produce an ethyl ester (commonly referred to as Fatty Acid Ethyl Ester FAEE)

CH_2COOR | | KOH | | CH_2OH

$CHCOOR + 3\,CH_3OH \xrightleftharpoons{KOH} 3CH_3COOR + CHOH$

CH_2COOR | | | | CH_2OH

Vegetable oil | | Biodiesel | Glycerol

The products are allowed to settle and from the bottom glycerol layer is drawn off. The upper layer of methyl ester is washed with water and purified further to remove excess of alcohol which finally gives biodiesel.

Cooking oil or animal fat can be converted into biodiesel. Since triglycerides undergo hydrolysis with water forming mono, diglycerides and free fatty acids , the direct esterification in the presence of alkali results in soap formation. It is avoided by first esterifying the free fatty acid in the presence of an acid catalyst followed by base catalyzed trans-esterification to produce biodiesel.

Advantages:

1. It is biodegradable, nontoxic and free from sulphur compounds.
2. Non edible oils can be used.
3. Ecofriendly products are formed.

FUEL CELLS:

A fuel cell is an electrochemical cell in which the energy of combustion of a fuel such as hydrogen, methane, carbon monoxide, methanol etc. is directly converted to electrical energy.

Comparison of fuel cells & a battery:-

Fuel cell	Battery
1.Reactions are fed from outside the cell (and not an integral part of the cell)	1. Reactants are an integral part of the battery
2. Chemical energy is not stored in the fuel cell.	2. Chemical energy is stored in the battery.
3. Fuel cells operate as long as reactants are supplied to the electrodes from the outside.	3. Battery operates until the reactants stored in it are completely used up.
4. There is no need to charge a fuel cell.	4. A secondary battery has to be recharged once it is almost used up.
5. Fuel cell has a very high efficiency.	5. Efficiency of a battery is low.

Advantages of fuel cells:

- Power output is high.
- Do not pollute the atmosphere.
- Electrical energy can be obtained continuously.
- High efficiency.
- Silent operation.
- No wear &tear.
- No need of charging.

Limitations of fuel cells:

- Cost of power is high as a result of the cost of the electrodes.
- Fuel is in the form of gases and oxygen need to be stored in tanks under high pressure.
- Power output is moderate.
- To have an appreciable voltage, a battery of fuel cells must be available.

Methanol-oxygen fuel cell:

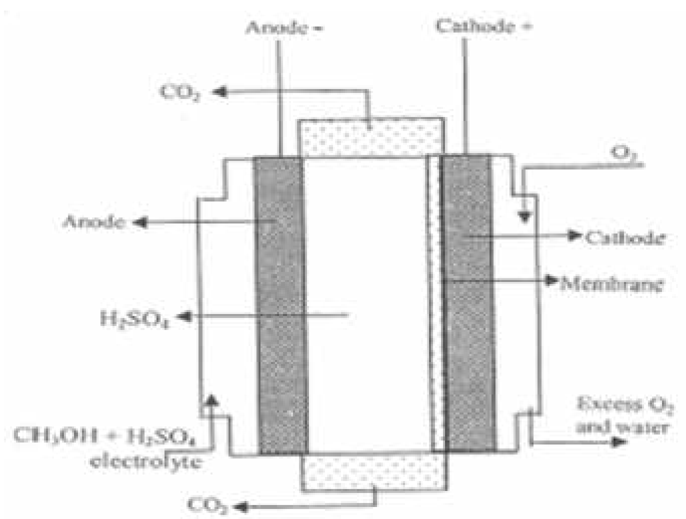
Construction and working:-

Anode: It is a porous nickel sheet on which platinum or palladium catalyst is deposited.

Cathode: It is a porous nickel sheet on which silver is deposited.

Electrolyte: Sulphuric acid.

Methanol is circulated through the anode chamber and oxygen gas is circulated through the cathode. A membrane is inserted close to the cathode to minimize diffusion of methanol into the cathode thereby reducing the concentration of methanol near the cathode. The reactions are given below



Anode: $CH_3OH+H_2O \rightarrow CO_2+6H^++6e^-$

Cathode: $3/2\ O_2+6H^++6e^- \rightarrow 3H_2O$

Overall reaction: $CH_3OH+3/2\ O_2 \rightarrow CO_2+2H_2O$

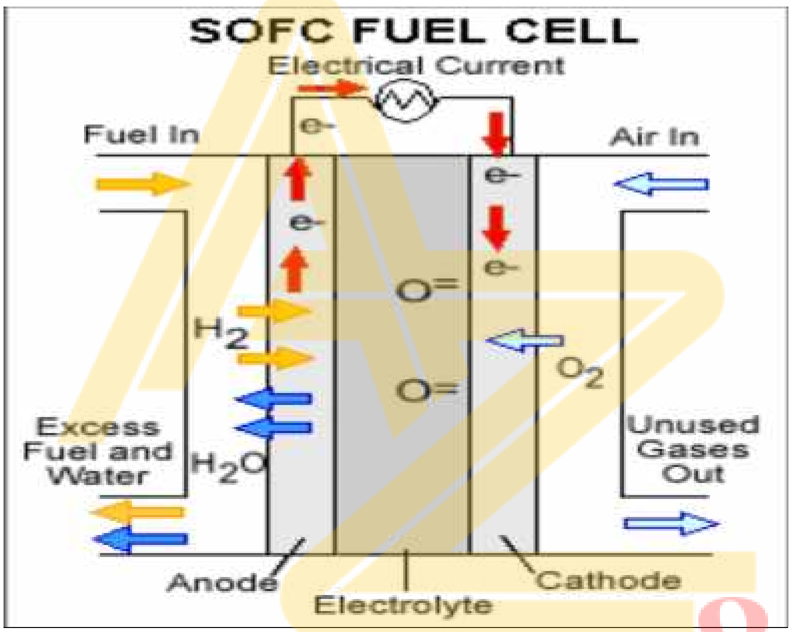
KOH is not used as electrolyte as it reacts with CO_2 and gets converted to carbonate.

Applications:

It is used in military applications and large scale power production.

Solid oxide fuel cells (SOFC):

These are a class of fuel cells which use a solid oxide material as the electrolyte. An SOFC consists of two porous electrodes separated by a dense, oxide ion conducting electrolyte. The operating principle of SOFC is illustrated in the following figure.



Oxygen supplied at cathode reacts with incoming electrons from the external circuit to form oxide ions(O^{2-}), which migrate to the anode through the electrolyte. At the anode, oxide ions combine with H_2 (and/or CO) in the fuel to form H_2O (and/or CO_2), liberating electrons. Electrons flow from anode through the external circuit to the cathode.

The electrode consists of a solid, nonporous metal oxide, typically ZrO_2 doped with Y_2O_3. The anode is made of CO ZrO_2 or Ni ZrO_2, while the cathode is made up of Sr doped $LaMnO_3$. The cell operates at 650^oC to 1000^oC such that conduction of oxygen ions through the electrolyte may occur.

The electrochemical reactions occurring within the cell are:

At Anode: $\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$

At Cathode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$

The overall cell reaction: $\frac{1}{2} O_2 + H_2 \rightarrow H_2O$

The CO and CH_4 can also be used as fuel in an SOFC. Both these produce H_2 which can be easily oxidized. When CO is used then the reaction will be:

$$CO + H_2O \rightarrow H_2 + CO_2$$

When natural gas is used then the reaction will be:

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

Application:-

1. Power systems in train, ships and vehicles.
2. Supplying electrical power for residential and industrial utility.

SOLAR ENERGY:

Solar energy is the energy which has a greatest potential of acting as a alternate source of enegy because of the reason that the reserves of fossil fuels are very limited and are depleted very fast.

Photovoltaic Cells: (Photo = sunlight, voltaic = electricity)

Definition: "*Photovoltaic cells or solar cells as they are often referred to are semiconductor devices that convert sunlight into direct-current electricity on illumination.*"

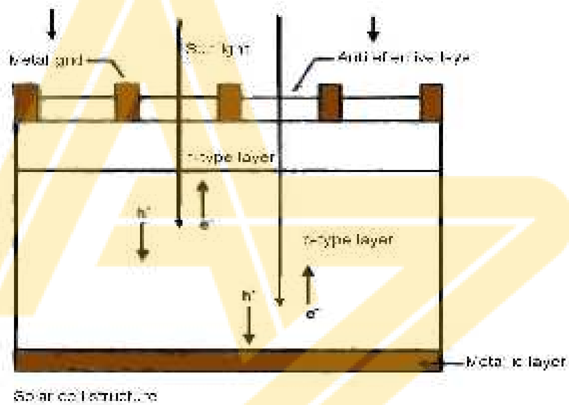
When semiconductors such as silicon are illuminated by photons (eg. From sunlight), electricity is generated. Electricity can be generated only as long as sunlight is available & in the absence of sunlight generation of electricity ceases. Solar cells never need recharging like a battery. Photovoltaic cells have no movable parts & hence do not suffer from wear & tear. They operate at ambient temperature, are environment friendly & do not corrode.

Construction of a photovoltaic cell & its working:-

Solar cells consist of p-n junction formed from a semi-conductor diode obtained when n-type & p-type semi conductor are brought together to form a metallurgical junction. The diode has two electrical contacts, one of which is in the form of a metallic grid & the other is a layer of nobler metal on the back of the solar cell. The metallic grid allows light to fall on the semiconductor between the gridlines to increase the amount of light transmitted through the front to the cell.

All electromagnetic radiations including sunlight consist of particles called photons. The photons carry a certain amount of energy given by $E = hc/\lambda$

Where h is Planck's constant, c is the velocity of light, λ is the wave length of radiation.
When electromagnetic radiation (sunlight) is incident normal to the plane of the solar cell, the photons which possess energy sufficient to overcome the barrier potential are absorbed & electron-hole pairs are formed. Electrons are driven out into the external circuit & could be stored & used for various applications.



Production of Solar grade silicon (crystalline):

<u>Metallurgical Grade</u> silicon is produced in submerged electrical arc furnace. The furnace consists of a crucible containing carbon and silica & an electric arc is struck. A high temperature is produced & silica is reduced to elemental silicon with a typical purity of 98.5%.

$$SiO_{2\,(s)} + 2C \rightarrow Si_{(l)} + 2CO_{(g)}$$

<u>Refining</u>: Elements less noble than silicon such as Al, Ca, & Mg are oxidized & <u>slag</u> is formed.

$$4\,Al + 3\,SiO_2 \rightarrow 3Si_{(l)} + 2Al_2O_3$$

$$2\,Ca + SiO_2 \rightarrow Si_{(l)} + 2CaO$$

$$2\,Mg + SiO_2 \rightarrow Si_{(l)} + 2MgO$$

The Si obtained is 99% pure and is called metallic grade Si.

Semiconductor grade silicon is used for solar cells. The purification of metallic grade silicon to obtain solar grade silicon involves the following steps.

(i) The metallic grade silicon is treated with dry HCl gas at 300^0C to form trichlorosilane & a small amount of tetrachlorosilane. The mixture is distilled to get pure trichlorosilane.

$$Si + 3HCl \rightarrow HSiCl_3 + H_2$$

$$Si + 4HCl \rightarrow SiCl_4 + 2H_2$$

Silicon tetrachloride is reduced with hydrogen at 1000^0C in a reactor

$$SiCl_4 + H_2 \rightarrow HSiCl_3 + HCl$$

(ii) Trichlorosilane, thus obtained is passed through fixed bed columns containing quaternary ammonium ion exchange resin as catalyst. Trichlorosilane gets converted into dichloro silane.

$$2HSiCl_3 \rightarrow \underset{\text{(Dichlorosilane)}}{H_2SiCl_2} + SiCl_4$$

The products are separated by distillation; tetrachlorosilane is recycled to the hydrogenation reactor.

(iii) Dichlorosilane is passed through a second fixed bed column filled with quaternary ammonium ion exchange resin. Dichlorosilane is converted into silane.

$$3H_2SiCl_4 \rightarrow SiH_4 + 2HSiCl_3$$

The above products are separated by distillation & trichlorosilane is recycled to the first bed column.

(iv) Silane is further purified by distillation & passed into a reactor containing heated silicon seed rods. Silane undergoes pyrolysis to give semiconductor grade silicon or polysilicon.

$$SiH4 \rightarrow Si + 2H_2$$

Adavantages of PV cells:

1. Fuel is vast and essentially infinite.
2. No emissions, no combustion or radioactive residues for disposal.
3. No moving parts and no wear and tear.
4. Quick installation.
5. Can be integrated into new or existing building structures.
6. High public acceptance and excellent safety record.

Disadvantages of PV cells:

1. Sunlight is a diffused source of light.
2. High Installation Cost
3. Energy can be produced only in the day time.