

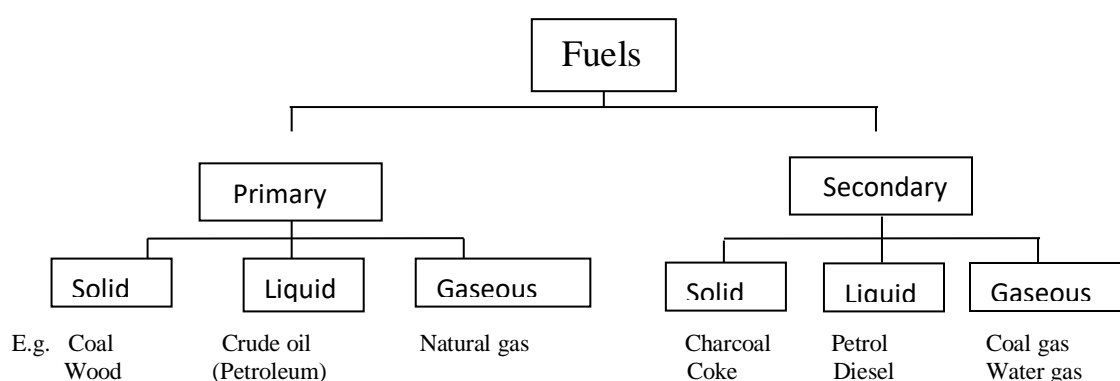
Chemical Fuels and Photo-Voltaic Cells

Introduction:

- Energy is the fundamental aspect of human life.
- Energy is defined as the capacity to do work.
- Everything we do is connected to energy in one form or the other. Chemical fuels are used in transportation, communication and illumination *etc.*,

Chemical fuels: It is defined as naturally occurring or artificially synthesized combustible carbonaceous material used mainly as source of light, heat and also a source of raw material.

Classification of fuels: On the basis of origin, fuels are classified as primary and secondary fuels.



Primary fuels: The fuel which is available in nature and doesn't require any chemical processing before utilization.

Ex: wood, coal, crude petroleum and natural gas.

Secondary fuels: The fuels which are not available in nature but produced from naturally occurring substances by subjecting to various treatments, which alter their chemical composition and improve their calorific value.

Ex: Coke, gas-LPG, Diesel, Petrol, Kerosene

Hydrocarbon fuels: The fuels which contain only hydrogen and carbon are called hydrocarbon fuels. Ex: Petrol, diesel, kerosene.

Calorific value of a fuel: It is measured in terms of heating efficiency. It is defined as the amount of heat evolved by the complete combustion of unit quantity (mass or volume) of the fuel in air or oxygen.

It is expressed in kJ/Kg for solid and liquid fuels and kJ/m³ for gaseous fuels.

Calorific values are expressed in two ways:

1. Gross calorific value (GCV)
2. Net Calorific value (NCV)

Gross calorific value (GCV): It is defined as the quantity of heat evolved by the complete combustion of unit quantity of the fuel in air or oxygen and the combustion products are brought down to room temperature. Most of the fuels contain carbon and hydrogen, on combustion carbon and hydrogen are converted into CO₂ and steam respectively. On cooling, the combustion product steam gets condensed to water and liberates its latent heat. Hence, GCV is the sum of heat of combustion of fuel and the latent heat of condensation of steam.

Therefore, GCV is always higher than the net calorific value.

Net Calorific value (NCV): It is defined as the quantity of heat evolved by the complete combustion of unit quantity of the fuel and the combustion products are let off into the atmosphere.

i.e., the combustion products are not cooled to room temperature but they are allowed to escape into the atmosphere. Hence, this calorific value does not include latent heat of steam. Therefore, Net calorific value is always lower than GCV.

NCV = [GCV – latent heat of condensation of steam]

$$\begin{aligned}\text{CV} &= [\text{GCV} - (0.09 \times \% \text{H}_2 \text{ in fuel}) \times L] \\ &= [\text{GCV} - (0.09 \times \% \text{H}_2 \text{ in fuel}) \times 2454] \text{ kJ/kg}\end{aligned}$$

Where, L = Latent heat of steam = 2454 kJ/Kg

Determination of calorific value of a solid or liquid fuel using Bomb Calorimeter:

Calorific value of solid or liquid fuel is determined by burning known mass of the fuel in excess of oxygen in a bomb calorimeter.

- It consists of strong cylindrical steel vessel with air tight screw lid and a valve for introducing oxygen.
- A known volume of the fuel in the form of pellets is taken in a ceramic or platinum crucible, with a loop of iron wire projecting outward is placed in the bomb.
- The lid is tightly closed and oxygen is pumped at a pressure of 25-30 atm.
- The bomb calorimeter is kept in a known quantity of water taken in another brass calorimeter.
- The brass calorimeter is enclosed with a jacket to minimise heat exchange with the surroundings.
- The initial temperature of water is noted using thermometer (t_1 K).
- The fuel is ignited by connecting the ends of the wire to a source of electric current. Rapid combustion of the fuel takes place. The heat evolved by the combustion is absorbed by water molecule, which is constantly stirred. The final temperature of the water is noted (t_2 K).
- Therefore, heat released by the fuel = heat absorbed by the water

$$\text{GCV (solid fuel)} = \frac{(W+w) \times (t_2 - t_1) \times s}{m}$$

m = mass of fuel

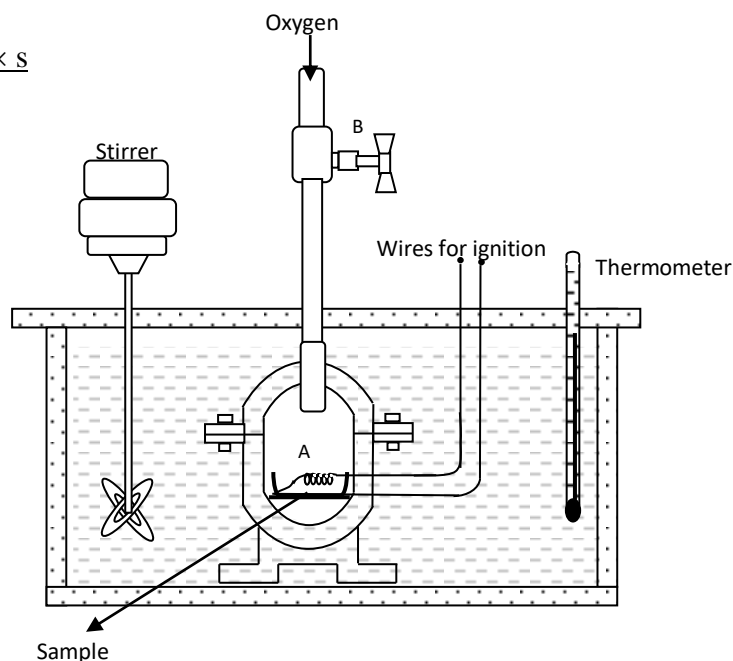
W = mass of water

w = water equivalent of calorimeter

t_1 = initial temperature of water

t_2 = final temperature of water

s = specific heat of water (4.187 kJ/kg/k)



Petroleum: It is naturally occurring substance made up of several hydrocarbons. It is found under the rocky strata of the earth crust. It is non renewable energy source as it takes millions of years to form. Petroleum is subjected to fractional distillation to get various fractions like petrol, diesel, kerosene etc.

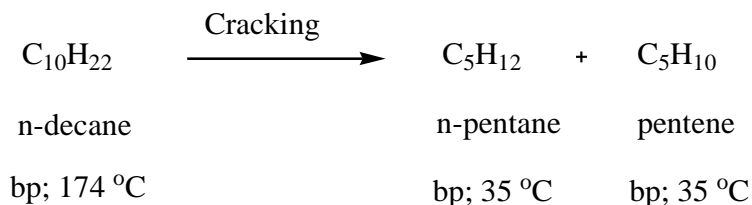
The process of separating various components of petroleum from one another having different boiling points and molecular weight is called fractional distillation and the process is known as refining of petroleum.

Chemical processing of petroleum: Fractional distillation of petroleum physically separates the fractions of crude oil into its constituent fractions. These fractions are further converted into useful products by subjecting to various chemical processes.

The two important chemical process used to achieve these objectives are

- Cracking
- Reforming

Cracking: The process of breaking up of high molecular weight hydrocarbons into more useful low molecular weight hydrocarbons in presence of heat but in the absence of oxygen is called cracking. This involves the change in molar mass.



There are two types of cracking process were recognised

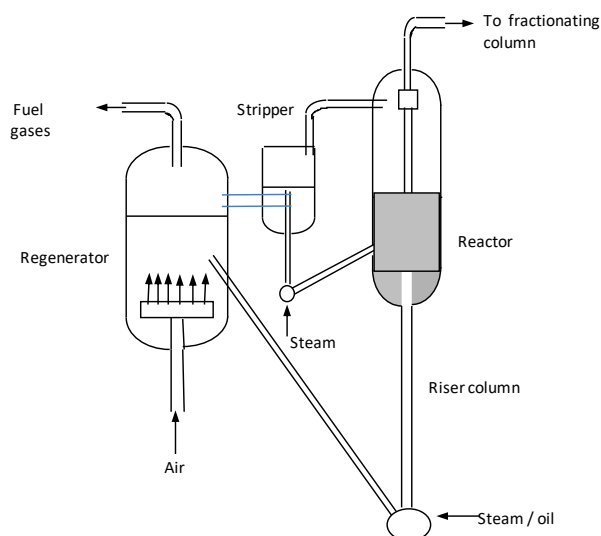
Thermal cracking: In this process petroleum is subjected to high pressure and temperature (700° C) in the absence of air and a catalyst. This method is not used since there is no control over the product of cracking and the efficiency is low.

Catalytic cracking: In this process petroleum is subjected to low pressure and temperature in presence of catalyst. This cracking process is control over the end products.

Fluidized catalytic cracking:

Working or method:

- In this process, oil is preheated to about 500° C is sprayed from the bottom into a riser column containing the catalyst.
- Oil mixes with powdered catalyst at 700° C, then it carries the catalyst and the oil mixture in a fluidized state into the reactor thereafter cracking takes place.
- Cracked products are taken and transferred into a fractionating column for further separation.
- The spent catalyst is pumped from the catalyst chamber into a regeneration chamber. Hot air is blown from the bottom of the chamber to burn the carbon deposit on the catalyst surface. The regenerated catalyst is sent back to the catalyst chamber and hence cracking process is continuous.



Advantages of the method:

1. The yield of synthetic petrol is higher
2. The quality of petrol produced is better
3. Low pressure at 1-5 kg/cm² is just sufficient for cracking
4. The cracking process can be controlled
5. Catalyst can be regenerated and used again
6. The product contains a very little amount of undesirable sulphur and posses better anti-knocking properties.

Knocking: The performance of motor car is measured in terms of Km/l of petrol, which depends on the quality of the fuel. Important method of obtaining more power from petrol is increasing the compression ratio of the engine.

$\text{Compression ratio of engine} = \frac{\text{Initial volume of petrol and air mixture sucked into cylinder}}{\text{Final volume of petrol and air mixture after compression}}$

The efficiency of the engine increases with increase in the compression ratio of the engine. The combustion reaction of the petrol is initiated by a spark; as a result flame spreads rapidly and smoothly through gaseous mixture in the cylinder. By this pressure increases inside the cylinder under thermal conditions.

The mixture of air and petrol suddenly bursts into flames beyond a particular compression ratio. This process is accompanied by a sharp knock in the internal combustion engine due to explosive combustion which resulting in shock wave. This shockwave lose its energy by hitting the walls of the cylinder and piston as a result a rattle sound is heard which is referred as knocking.

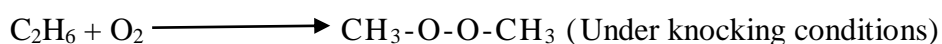
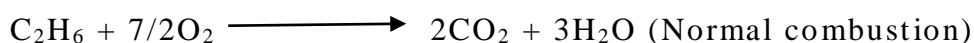
“Knocking is defined as the production of shock wave in an IC engine due to explosive combustion of mixture of petrol and air which increases compression ratio beyond a certain value leading to rattle sound”.

Affects of Knocking: Knocking causes the following effects

1. Produces undesirable rattling sound
2. Decreases efficiency of engine and power out-put
3. Increases the fuel consumption
4. Causes the mechanical damage to engine parts
5. The driving becomes rather unpleasant

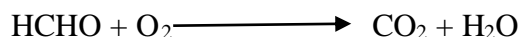
Mechanism of Knocking:

- Under ideal conditions, the oxidation of fuel takes place slowly during which oxygen combines with a few hydrocarbon molecules and activates them.
- The activated hydrocarbon molecules combine with other hydrocarbon molecules set up a chain reaction resulting in the smooth combustion.
- In case of knocking conditions, all the hydrocarbon molecules activated rapidly and they combine at a faster rate to set up a chain reaction results in explosive combustion. Hence knocking occurs.
- The knocking is due to the formation of unstable peroxide which decomposes rapidly to give a number of gaseous compounds. This give rise to pressure waves inside the cylinder which knocks against the engine walls.



Fuel

Ethane peroxide



Octane number and Cetane number:

The knocking characteristics of petrol sample are described by the octane number. Higher the octane number lower is the tendency to knock and better is the quality of the petrol.

Isooctane (2,2,4-trimethyl-pentane) has least knocking tendency and its octane number is arbitrarily fixed as 100. N-heptane a straight chain hydrocarbon has the highest tendency to knock and its octane number is fixed as 0.

Therefore, octane number is defined as the % of isooctane present in a standard mixture of isooctane and n-heptane which knocks at the same compression ratio as the petrol being tested.

Cetane number:

Quality of petrol sample is expressed in terms of its octane number; where as the quality of diesel is expressed by means of Cetane number.

Cetane or hexadecane ($C_{16}H_{34}$) is an ideal fuel with a Cetane number 100 and α -methyl naphthalene has a Cetane number of zero.

“Cetane number is defined as the % of hexadecane present in a standard mixture of Cetane and α -methyl naphthalene which knocks at the same compression ratio as the diesel being tested.

Anti-knocking agents:

The substances added to control knocking is called as anti-knocking agents and these substances improve the octane number of petrol.

Tetra ethyl lead (TEL) [$Pb (C_2H_5)_4$]: TEL acts as anti-knocking agent it reacts with peroxy compounds and decomposes them thereby prevents knocking.

Lead containing anti-knocking agents is extremely damaging to the environment and so it is advisable to use unleaded petrol like methyl tertiary butyl ether (MTBE).

Methyl Tertiary Butyl Ether (MTBE): It acts as anti-knocking agent which contains ‘O’ in the form of ether group and supplies ‘O’ for the combustion of the petrol in IC engine thus reduces the formation of peroxy compounds.

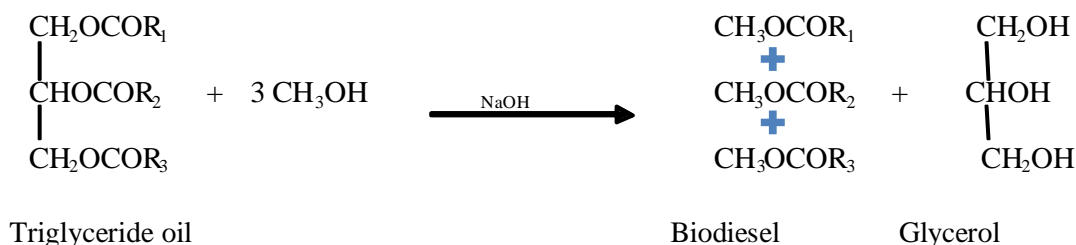
Biodiesel: It is a mixture of long chain mono alkyl esters of fatty acids derived from vegetable oils or animal fat.

Biodiesel is non-toxic, biodegradable, replacement for petroleum diesel. Chemically biodiesel is a fatty acid monoalkyl ester.

The oil / fat are triglycerides esters of fatty acids and their use in engine requires extensive engine modifications. However, it is possible to convert these triglycerides into substance of diesel quality by transesterification.

“Transesterification is alcoholysis of the triglyceride oil in the presence of a base like NaOH to obtain biodiesel. Thus, biodiesel is a mixture of mono alkyl esters of long chain fatty acids.

The transesterification of triglyceride oil with methanol in presence of NaOH is given below:



The direct transesterification in presence of alkali results in the formation of soap. This soap forms a semi solid mass at ambient temperature and affects the engine performance. It also affects the separation of glycerol from diesel layer.

This soap formation is avoided by first esterifying the free fatty acid in presence of an acid catalyst. This is followed by base catalyzed transesterification to get biodiesel. The transesterification proceeds at RT but the rate can be increased by raising temperature to 60° C.

Advantages of biodiesel:

- It is made using renewable sources and feed stocks
- Readily undergoes biodegradation, nontoxic, suitable for sensitive environments.
- It has higher flash point than the diesel but lower ignition point.
- It has higher cetane number (48-60) compared to diesel (40-55)
- Use of biodiesel reduces green house gases.

Power alcohol:

A mixture of ethyl alcohol and gasoline blend, which can be used as fuel in internal combustion engines known as power alcohol or gasohol.

Absolute alcohol is mixed with ether, benzene etc., compounds and one volume of this is mixed with four volumes of petrol is used as a fuel.

“Ethyl alcohol is used as an additive to motor fuels to act as a fuel for IC engines and it is called as power alcohol.”

Advantages:

- The power out put is good.
- It has better antiknock property.
- Ethanol is biodegradable; hence it is environmental friendly fuel.
- The use of ethanol in alcohol increases the oxygen content of the fuels and promotes complete combustion of hydrocarbons in gasoline.
- It reduces poisonous carbon monoxide emission

Solar Energy:

The present dominant energy sources are petroleum, natural gas, hydro power and nuclear energy. These energy sources are very limited and are being depleted very fast as a result search for alternative sources of energy has gained lot of importance. The world is looking towards the natural resources such as solar energy, wind energy, etc., among these, solar energy is the potential candidate. The energy supplied by this is enormous, continuous and free of cost. Solar energy provides heat and light, therefore in last few decades lot of effort has been made towards the use of solar energy.

The device which is used to convert heat energy of the sun into electrical energy is called solar cells or photo voltaic cells.

Doping of Silicon by Diffusion Technique:

In this technique, semi conductor material is incorporated with different dopants into the crystal without melting the material. By the above technique, the extent of impurity penetration can be controlled to a very small thickness of the material. For example, a n-type silicon can be obtained by heating a silicon wafer below its melting point in an atmosphere of n-type impurity such as Phosphorus.

The valency of silicon is 4, when pentavalent impurity like phosphorus is doped into silicon it provides five valence electrons. Out of 5 valence electrons of phosphorus four will combine with four valence electrons of silicon atom to form bonds. There is an extra electron other than the electrons involved in bonding. This extra electron is treated as negative charge. This makes the silicon n-type semiconductor. The impurity atoms condense on the surface of the wafer diffuse into the crystal.

P-type silicon can be obtained by heating a silicon wafer below its melting point in an atmosphere of P-type impurity such as Boron. The valency of silicon is 4, when trivalent impurity like boron is doped into silicon it provides three valence electrons. These electrons combine with three valence electrons of silicon atom to form covalent bonds. There is a shortage of electron for the silicon atom to form another covalent bond. This shortage of electron is treated as hole. This makes silicon p-type semiconductor. The extent of diffusion is regulated by temperature and concentration of the impurity atom.

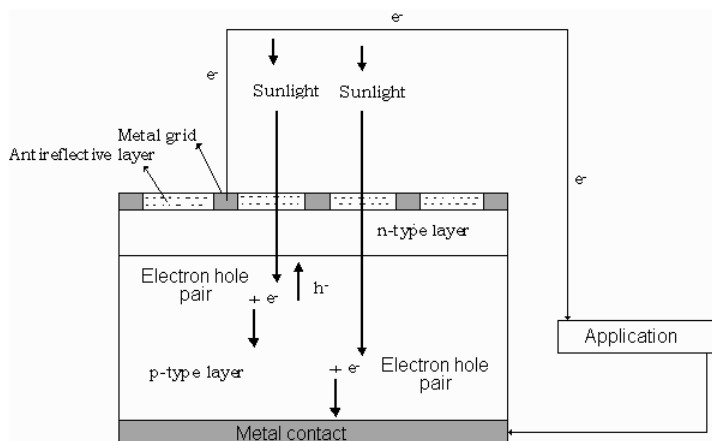
Photo-Voltaic cells:

They often referred as semiconductor devices that convert solar energy into electrical energy.

Construction and Working of Photo-Voltaic cells:

Semiconductors like silicon have the capacity to absorb light and deliver a portion of the energy of the absorbed photons to carry charge carriers (electrons and holes). Thus solar cell is a semiconductor diode that has been designed carefully so that it can absorb the light energy efficiently and convert light energy from the sun into electrical energy.

A conventional solar cell structure is shown in figure:



Construction: A typical silicon photo voltaic cell composed of thin layer of phosphorus doped silicon (n-type) on top of boron doped (p-type) silicon and hence these two layers form p-n junction diode.

A metallic grid is the electrical contact between the diode and allows light to fall on the semiconductor between the grid lines. An antireflective layer between the grid lines increases the amount of light transmitted to semiconductor.

Working: When light radiation falls on the p-n junction diode, electron-hole pairs are generated by the absorption of radiation. The electrons are diffused and collected at the n-type end and holes are diffused and collected at the p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends through the external circuit which results in photoelectric current and available for use.

Physical properties of silicon relative to photovoltaic cells:

- Silicon is a semiconductor with band gap of 1.2eV at 25°C.
- At atmospheric pressure, silicon crystallizes to diamond cube like structure.
- Silicon contracts when melted and expand when solidify.
- High refractive index limits the optical applications of silicon.
- The absorption and transmission properties in the 0.4-0.5 μm wavelength spectra are important in the performance of photovoltaic cells.

Chemical properties of silicon relevant to photovoltaic's:

- Silicon is stable in the tetravalent and has a strong affinity for oxygen, forming stable oxides and silicates.
- Silicon and carbon form a strong Si-C (silicon carbide) bond and stable products.
- Silicon forms hydrides, and monosilanes (SiH_4) is key chemical compound for the production of amorphous silicon and the purification of silicon to semiconductor grade.
- Silicon forms trichlorosilane and tetrachlorosilane with chlorine, which are the intermediates and the by-products of the purification process in metallurgical grade silicon to semiconductor grade.

Importance of Photovoltaic cell:

- Photovoltaic cell provides enormous amount of energy from sun which is unlimited, inexhaustible and renewable.
- Photovoltaic cells can serve for both off grid and on grid application.
- Photovoltaic cell produces no pollution so it is environment friendly.

- Photovoltaic cell energy conversion is highly modular. This is important with respect to the development of electricity supply systems in many rural and remote areas, where grid extension is economically not feasible.
- It provides power for space craft and satellite.
- Photovoltaic's can be used as roof integrated systems, providing power and also serving as optical shading elements for the space below and preventing overheating in the summer.
- Developments in the field of Photovoltaic cells will boost the semiconductor industry and storage battery industries.

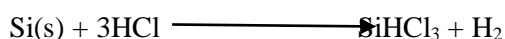
Production of solar grade silicon:

Silicon is obtained by reducing silicon dioxide (SiO_2) with coke in an electrode arc furnace at about $1300\text{--}2000^\circ\text{C}$.

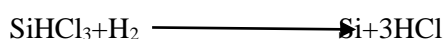


The obtained liquid silicon collects at the bottom of the furnace. Then it is dried and cooled. The silicon obtained by this process is called metallurgical grade silicon and its purity is 98 %. This metallurgical grade silicon is not suitable for semiconductor devices. It demands greater purity than the metallurgical grade silicon.

To get high purity silicon, metallurgical grade silicon is refined by treating it with anhydrous HCl at 300°C in a fluidized bed reactor to form trichlorosilanes (SiHCl_3).

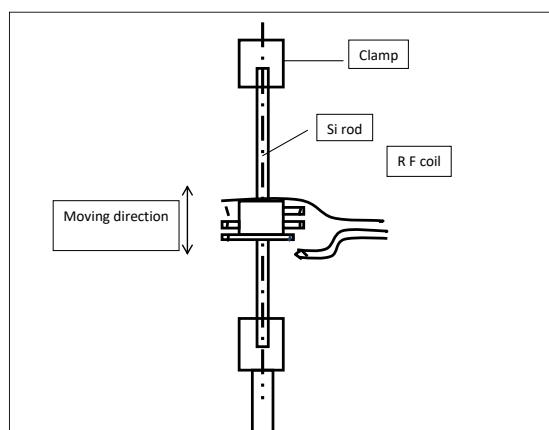


Trichlorosilanes has low boiling point of 31.8°C , therefore it is purified by fractional distillation to remove halide impurities (FeCl_3 , AlCl_3 , BCl_3). In the next step, lighter impurities like Al, B, P, Fe, Cu are eliminated. Finally, pure SiHCl_3 is treated with hydrogen at 1100°C for 200-300 hrs to produce a very pure form of silicon. This process is often referred to as Siemens process.



Purification of silicon (Zone refining)

The principle of zone refining is that when a solid is melted, the impurities tend to concentrate in the molten zone.



A vertical zone refiner is used in the purification of silicon. A rod of silicon to be purified is clamped as shown in figure and is heated by a RF coil to the melting point of silicon in the presence of argon gas. The heater is moved very slowly from top to bottom. This is said to be one zone pass. Impurities move with the molten part of the material as the RF coil moves down. Pure silicon solidifies at the upper portion. When the process is complete, the bottom portion where the impurities are concentrated is removed. The rod is subjected to several zone passes to get ultrapure silicon.

Assignment Questions

1. What are chemical fuels and define a) Calorific value b) Gross calorific value and c) Net calorific value
2. How calorific value of a fuel is determined by bomb calorimeter?
3. What is cracking? Explain with a neat labelled diagram fluidized catalytic cracking.
4. What is knocking? Explain the mechanism of knocking and disadvantages of knocking.
5. Define: a) Octane number b) Cetane number c) Power alcohol.
6. What is biodiesel? How is it prepared? What are the advantages?
7. What are photovoltaic cells? Explain the working and construction of photovoltaic cells.
8. Discuss the advantages and disadvantages of photovoltaic cells.
9. Explain the method for the production of solar grade silicon.
10. Explain the purification of silicon by zone refining.
