UNIT: II **(DISTILLATION)**

CLASS:20

## TOPIC: STEAM DISTILLATION & MOLECULAR DISTILLATION

## STEAM DISTILLATION

*Steam distillation* is a method of distillation carried with the aid of steam and is used for the separation of high-boiling substances from non-volatile impurities.

High-boiling liquids cannot be purified by simple distillation, since the constituents in the mixture tend to decompose at higher temperatures. In such cases, steam distillation is employed. Steam distillation is used for the separation of immiscible liquids.

For substances, which are insoluble in water and not decomposed by heat, steam distillation provides an alternative to distillation under reduced pressure. Steam distillation is the most common example of differential distillation.

Principle: A mixture of immiscible liquids begins to boil when the sum of their vapour pressures is equal to the atmospheric pressure. In case of a mixture of water and turpentine, mixture boils below the boiling point of pure water, though the turpentine boils at a much higher temperature than that of water.

For example, the boiling point of turpentine is about 160°C. But when it is mixed with water and heated, the mixture boils at about 95.6°C. At this temperature, the vapour pressure of water is 86.245 kPa (647 mm Hg) and that of turpentine is i5.06 kPa (1 13 mm Hg). The sum of the vapour pressures is 101.31 kPa (760 mm Hg) which is normal atmospheric pressure. Thus, high boiling substances may be distilled at a temperature much below its boiling point, when water (steam) is used. For volatile substances. which are miscible with water, steam distillation involves the same principle as fractional distillation.

**Applications** (1) Steam distillation is used for the separation of immiscible liquids. Example is toluene and water.

(2) This method is used for extracting most of the volatile oils such as clove, anise and eucalyptus.

(3) It is useful in purification of liquid with high boiling point, for example essential oil of almond.

(4) Camphor is distilled by this method.

(5) Aromatic waters are prepared. by this method.

**Advantages**: Volatile oils can be separated at a lower temperature in . steam distillation, without any decomposition and loss of aroma. If a substance has low volatility, it can be satisfactorily distilled. provided its molecular weight is considerably higher than water.

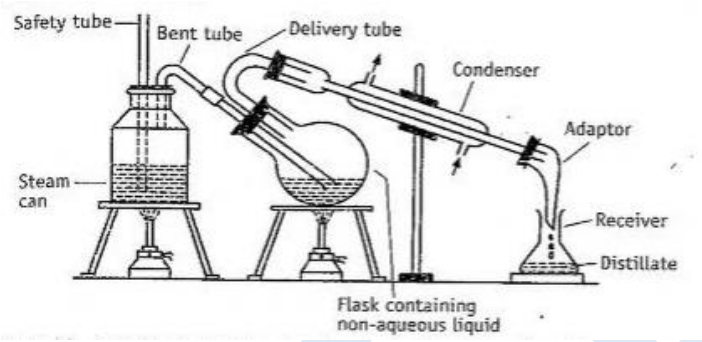
**Disadvantages**: Steam distillation is not suitable when immiscible

liquid and water react with each other

**Apparatus Used for Laboratory Scale**

**Assembly of apparatus**: The assembly of apparatus for steam distillation on laboratory scale is shown in Figure.

It consists of a metallic 'steam can' fitted with a cork having two holes. Through one of the holes, a long tube is passed so as to reach almost the bottom of the steam generator. This tube acts as a safety tube, so that in case the pressure inside the steam generator becomes too much, water will be forced out of it and the pressure will be relieved. Moreover, when steam starts coming out from the safety tube, it indicates that the steam can is almost empty. Through another hole, a bent tube is passed. The other end of the bent tube is connected to the flask containing non-aqueous liquid (for example, crude containing volatile oil) through a rubber bung.




Assembly of apparatus for steam distillation (on laboratory scale).

This tube should reach almost the bottom of the flask. Through the other hole of the rubber bung, a delivery tube is inserted which connects the flask and the condenser. The condenser is connected to a receiver flask using an adaptor. Provisions are made to heat the steam can and flask.

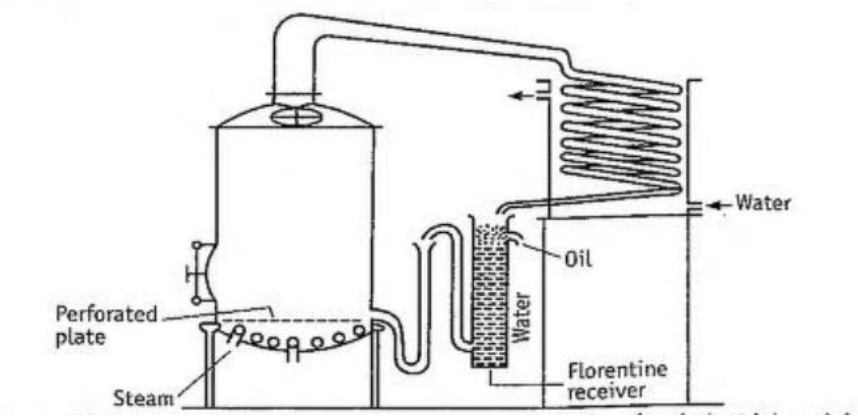
**Procedure**: The non-aqueous liquid is placed in the flask. A small quantity of water is added to it. Steam can is filled with water. The steam generator and the flask are heated simultaneously, so that a uniform flow of steam passes through the boiling mixture. The mixture gets heated. The steam carries the volatile oil and passes into the condenser, which is cooled by cold water. The condensed immiscible liquid is collected into the receiver.

Distillation is continued until all the non-aqueous liquid has been distilled. In the receiver, water and organic liquid form two separate layers, which can be easily separated using a separating flask.

For volatile substances, which are miscible with water, distillation with steam would involve the same principle of fractional distillation.

### Equipment Used on Industrial Scale

**Construction**:




Assembly of apparatus for steam distillation (on industrial scale)

Steam distillation unit is diagrammatically shown in Figure. It consists of a jacketed still with a perforated plate which forms a false bottom. Manholes are provided at the top and side for charging and discharging. A Florentine receiver is placed between the still and condenser. The condenser is cooled by circulating cold water

**Working**: The material from which the volatile oil has to be extracted is placed in the still above the perforated plate. Steam is admitted to the jacket of the still. The water and material present in the still are heated to boiling. Simultaneously steam is also injected below the materials through a steam pipe from the jacket. The steam carries the volatile oil and gets condensed in the condenser. which is cooled by cold water. The condensate is collected into the Florentine receiver. Most volatile oils are lighter than water and well separated from the distillate as an upper layer and removed from the upper spout.. The water can run off from the spout on the left and returns to the still.

Some volatile oils are heavier than water in which case the separation is reversed. Oil is collected from the lower spout.

**Variants** :(1) For volatile substances, which are miscible with water, distillation method combines the principles of the steam and fractional distillations.

(2) If the specific gravity of the oil is near 1.0, then separation does not take place. In such cases. it may be necessary to collect the whole of the distillate. Further it is extracted with an (volatile) organic solvent. The solvent should be distilled off to get the volatile oil.

## MOLECULAR DISTILLATION

*Molecular distillation* is defined as a distillation process in which each molecule in the vapour phase travels mean free path and gets condensed individually without intermolecular collisions on application of vacuum.

Molecular distillation is based on the principle of the simple distillation with some modifications. This is also called evaporative distillation or short path distillation.

**Principle**: The substances to be distilled have very low vapour pressures. Examples are viscous liquids, oils. greases, waxy materials and high molecular weight substances. These boil at very high temperatures. In order to decrease the boiling point of the liquids. high vacuum must be applied.

The vapour pressure above the liquid is much lower than that of the saturated vapour in equilibrium. At very low pressure, the distance between the evaporating surface and the condenser is approximately equal to the mean free path of the vapour molecules. Molecules leaving the surface of

the liquid are more likely hit the condenser surface than to collide with other molecules. Little or no re-condensation takes place at the surface of the liquid.

**Applications**: Molecular distillation is used for the purification and separation of chemicals of low vapour pressure.

(1) Purification of chemicals such as tricresyl phosphate, dibutyl phthalate and dimethyl phthalate.
(2) More frequently used in the refining of fixed oils.

(3) Vitamin A is separated from fish liver oil. Vitamin E is concentrated by this method from fish liver oils and other vegetable oils.

(4) Free fatty acids are distilled at 100°C. Steroids can be obtained between 100°C and 200°, while triglycerides can be obtained from 200°C onwards. Proteins and gums will remain as non- volatile residues. Thus, the above mixture can be separated by molecular distillation.

Theory: The mean free path of a molecule is defined as the average distance through which a molecule can move without coming into collision with another.

The mean path (λ) can be expressed mathematically as:

$$\lambda = \eta \sqrt{\frac{3}{P\rho}}$$

p = vapour pressure, kPa

ρ = density. kg/m3

η = viscosity, Pa's

A = mean path length, m

For example. mean path (heavy molecules) of butyl phthalate is about 30 mm and of olive oil is 20 mm when measured at a pressure of 0.I pascal.

The characteristics of the substance influence the method of distillation. According to equation

(a) Liquids having low viscosity and density posses long mean path. Distillation is simple.

(b) Substances having high pressures possess low mean free path.

The mean free path can be increased by decreasing the viscosity (η). which can be obtained at high temperature and low pressure. Thus, non-volatile substances may become volatile and distillation is possible. It is necessary to design the equipment based on the requirement of the molecular distillation. Some of them are as follows.

(1) The evaporating surface must be close to the condensing surface. This ensures the molecules to come in contact with the con-denser as soon as they leave the evaporating surface. For this reason, this process is also known as short path distillation.

(2) The molecular collisions should be minimized because they change the direction of the path of molecules. In other words, intermolecular distances should be fairly high. It can be achieved under very high vacuum, usually of the order of 0.1 to 1.0 pascals.

(3) The liquid surface area must be as large as possible so that the vapour is evolved from the surface only, but not by boiling. Thus this process is also called evaporation distillation.

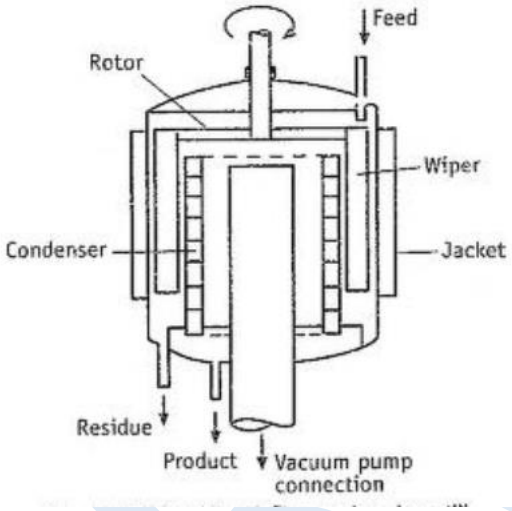
Based on the method of formation of the liquid film, apparatus may be divided into two types.

### Falling Film Molecular Still or Wiped Film Molecular Still

**Principle**: In this method, vaporisation occurs from a film of liquid flowing down a heated surface under high vacuum.

The vapour (molecules) travels a short distance and strikes the condenser nearby. Each molecule is condensed individually. The distillate is subsequently collected.

**Construction**: The construction of a wiped film molecular still is shown in Figure. The vessel has a diameter of one metre. The walls of the vessel are provided with suitable means of heating (jacket). Wipers are provided adjacent to the vessel wall. Wipers are connected to a rotating head through a rotor. The condensers are arranged very close to the wall (evaporating surface) as shown in Figure. Vacuum pump is connected to a large diameter pipe at the centre of the vessel. Provisions are made for collecting the distillate and the undistilled liquid residue at the bottom.



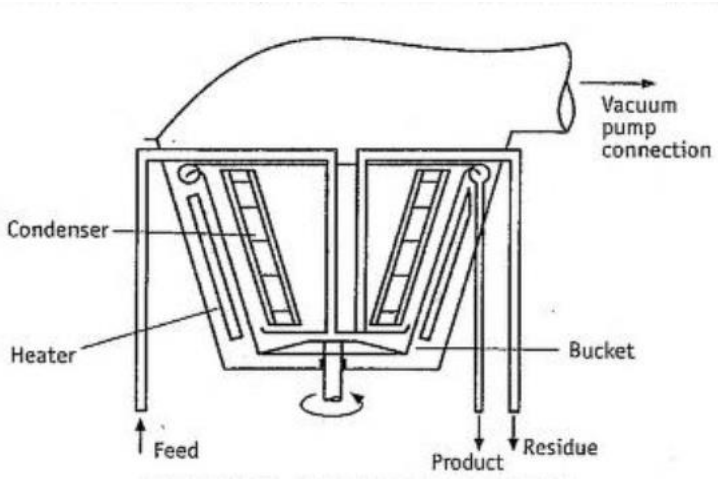

Wiped film molecular still.

**Working**: The vessel is heated by suitable means. Vacuum is applied at the centre of the vessel and wipers are allowed to rotate. The feed is entered through the inlet of the vessel. As the liquid flows down the walls. it is spread to form a film by PTFE' (polytetrafluoroethylene) wipers, which are moving at a rate of 3 metre per second. The velocity of the film is 1.5 metres per second. Since the surface is already heated, the liquid film evaporates directly. The vapour (molecules) travels its mean free path and strikes the condenser. The condensate is collected into a vessel. The residue (undistilled or mean free path not travelled) is collected from the bottom of the vessel and re-circulated through the feed port for further distillation. Capacity is about 1000 litre per hour.

### Centrifugal Molecular Still

**Principle**: In this method, liquid feed is introduced into a vessel, which is rotated at very high speed (centrifugal action). On account of heating. vaporisation occurs from a film of liquid on the sides of the vessel. The vapour (molecules) travels a short distance and gets condensed on the adjacent condenser. Each molecule is condensed individually. The distillate is subsequently collected.

**Construction**: The construction of a centrifugal molecular still is shown in Figure. It consists of a bucket-shaped vessel having a diameter of about 1 to 1.5 metre. It is rotated at high speed using a motor. Radiant heaters are provided externally to heat the fluid in the bucket.




Centrifugal molecular still.

Condensers are arranged very close' to the evaporating surface. Vacuum pump is connected to the entire vessel at the top. Provisions are made for introducing the feed into the centre of the bucket, for receiving the product and residue for re-circulation.

**Working**: Vacuum is applied at the centre of the vessel. The bucket shaped vessel is allowed to rotate at high speed. The feed is introduced from the centre of the vessel. Due to centrifugal action of the rotating bucket. liquid moves outward, over the surface of the vessel and forms a film. Since, the radiant heaters heat the surface, the liquid evaporates directly from the film. The vapour (molecules) travels its mean free path and strikes the condenser. The condensate is collected into another vessel. The residue is collected from the bottom of the vessel and is re circulated through the feed port for further distillation.

**Disadvantages**: Construction and operation are more complicated compared to falling film molecular still.

## DESTRUCTIVE DISTILLATION

Destructive distillation is a distillation method in which the distillate is decomposition products of the constituents of the organic matter burnt in the absence of air.

This process, is also known as dry distillation. It is not useful in laboratory practice. but one of the most important, industrial processes for obtaining many valuable products from wood, coal, and animal matter. It involves the heating of dry organic matter in a suitable vessel in the absence of air, until all volatile substances are driven off. The distillate is the decomposition products. Wood distillation industry' and coal carbonisation industry provide many useful materials.

## COMPRESSION DISTILLATION

Compression distillation method was developed to meet the needs of Navy and Army for fresh water, which is obtained from sea-water. The product obtained is quite pure and pyrogen-free. Therefore, it meets the requirements of the pharmaceutical industry. It is economical from the standpoint of consumption of fuel and water.

The feed water is heated in an evaporator for boiling. The vapour produced in the tubes is separated from entrained distilland in a separator. The vapour is then conveyed to a compressor, which compresses it and raises its temperature to about 118°C. It then flows to the steam chest where it is

condensed on the outer surface of the tube. During condensation, heat is released which is allowed for heating of the fresh feed in the tubes to the boiling point. The vapour is condensed and .drained off as disti!late.

**MCQ Each carry 1 mark**

1. What are the applications of steam distillation?
    a) Extract the inorganic compounds
    b) To clean the equipment
    **c) Extract and isolate essential oils**
    d) To purify drinking water
2. What is the advantage of steam distillation?
    **a) Reduces decomposition of temperature-sensitive compounds**
    b) Reduces decomposition of inorganic compounds
    c) Increases the decomposition of temperature-sensitive compounds
    d) Increases the decomposition of inorganic compounds
3. Which of the following statements about steam distillation are correct?
4. Statement 1: It cannot be applied under low pressure.
5. Statement 2: Used in isolation of organic compounds.
    **a) True, False**
    b) True, True
    c) False, True
    d) False, False
6. The organic liquid in steam distillation vaporizes at _____
    **a) Lower temperature than its boiling point**
    b) Higher temperature than its boiling point
    c) At its boiling point
    d) None of the mentioned
7. In steam distillation, the liquid boils when the sum of vapour pressure due to organic liquid and due to water becomes _____
    a) Greater than atmospheric pressure
    b) Lesser than atmospheric pressure
    **c) Equals to atmospheric pressure**
    d) None of the mentioned
8. **Molecular distillation is**
    **A.** High temperature distillation
    **B.** For heat-sensitive materials
    **C.** Very low pressure distillation
    **D.** Both B and C

**Each carry 5 marks**

1. What is meant by steam distillation? What are its special advantages?
2. Describe the principles and applications of steam distillation.

**Each carry 10 marks**

1. Explain the principle and procedure of molecular distillation. What are its applications?
2. Write about steam distillation