TRAINING MANUAL ON EXTRACTION TECHNOLOGY OF NATURAL DYE & AROMA THERAPY AND CULTIVATION VALUE ADDITION OF MEDICINAL PLANTS

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GETTING FRAGRANCE FROM PLANTS

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Introduction

Natural essential oils are the volatile, odoriferous oils obtained from plants. These are found in special cells, glands or ducts located in different parts of a plant such as the leaves, barks, roots, flowers and fruits and sometimes in just one or two parts. The oils are usually present in very small amounts and comprise only a tiny fraction of the entire plant material. The oils are produced during some metabolic processes of the plant and are secreted or excreted as odoriferous by-products. The fragrant oils may not necessarily be present as such in the living plants but may occur as odorless compounds termed as glycosides. When the plant tissues are macerated an enzymatic reaction occurs which causes the glycosides to undergo a chemical change. This action in turn liberates the distinctive essential oil. Essential oils are isolated from various plant parts such as leaves (patchouli), fruit (mandarin), bark (cinnamon), root (ginger), grass (citronella), wood (amyris), heartwood (cedar), gum (myrrh oil), balsam (tolu balsam oil), berries (pimento), seeds (dill), flowers (rose), twigs and leaves (thuja oil) and buds (cloves). The essential oil consists mainly of monoterpenes, sesquiterpenes and other chemical components of low molecular weight Limonene, camphor, α-pinene, β-pinene, cineole, camphene, Δ^3-carene, germacrene, eudesmol, caryophyllene are some of the examples.

Occurrence of Essential Oils

Occur in about 60 plant families. Following families reported to contain considerable EO:

Annonaceae	Cupressaceae	Lauraceae	Pinaceae
Asteraceae	Graminae	Orchidaceae	Rutaceae
Burseraceae	Geraniaceae	Myrtaceae	Vrbenaceae
Compositae	Labiatae	Piperaceae	Zingiberaceae

Important Source Plants of Essential Oils

Plant sources and important constituents of some common essential oils are as under

Sl. No.	Common Name	Botanical Name	Plant part used	Important Constituents	Uses
1.	Lemongrass and Citronella	*Cymbopogon spp*	Leaf	Citral Citronella Terpenes	Perfumery, Disinfectant
2.	Eucalyptus	*Eucalyptus globulus, Eucalyptus citriodora, Eucalyptus dives*	Leaf	Cineale, Citronella, Terpenes	Decongestant
3.	Cinnamon leaf	*Cinnamomum zeylanicum*	Leaf	Eugenol, Eugenol acetate, Cinnamic aldehyde	Used to make artificial vanilla. Flavouring
4.	Clove	*Eugenia caryophyllus*	Bud	Eugenol	Dentistry, Flavouring
5.	Turpentine	*Pinus spp*	-	Terpenes	Paints
6.	Lavender	*Lavendula intermedia*	Flower	Linalol	Perfumery
7.	Sandalwood	*Santalum album*	Wood	Sanatols	Perfumery
8.	Nutmeg	*Myristica fragrans*	Nut	Myristicin	Flavouring
9.	Almond	*Prunis communis*	Nut	Benzaldehyde	Flavouring
10.	Coriander	*Coriandrum sativum*	Seed	Linalol, Terpenes	Flavouring

RECOVERY OF ESSENTIAL OIL

Essential oils are volatile oils distilled from plant materials and represent the typical flavour and aroma (the essence) of a particular plant. They are found in flowers, leaves, roots, seeds and barks and find use principally in perfumery and flavourings. The essential oil content of plant material is low, typically 1 to 3% of the plant weight. They are thus low-volume, very high value products. This makes them attractive crops for remote smallholders where high transport costs prevent the transport of lower value cash crops. Essential oils contain a complex mix of components and it is this mix that gives the "note" that experts recognize.

The quality of the oil obtained from a particular species will be influenced by where it is grown and how it has been processed. New producers are likely to meet with resistance from buyers as this is a very conservative market depending to a great extent on trust regarding supply and quality. Producers and buyers also closely guard information and "secrets". Once established trading relationships are made, however, reliable markets can be gained. Essential oils can be divided into two broad categories:

- Large volume oils which are usually distilled from leafy material such as lemon grass, citronella and cinnamon leaves. Lemon, lime and orange oils are also produced in very large amounts.
- Small volume oils which are usually distilled from fruits, seed, buds and, to a lesser extent, flowers, e.g. cloves, nutmeg, coriander, vetiver and flower oils.

CORRECT HARVESTING FOR BETTER YIELD

Correct harvesting is very important. The essential oil content varies considerably during the development of the plant and even the time of day. If the plant is harvested at the wrong time, the oil yield or its quality can be severely reduced. Essential oils are usually contained in oil glands, or veins that are fragile. Poor handling will break these structures and release the oils resulting in losses. This is the reason a strong smell is given off when these plants are handled.

Some examples of harvesting of common oils are:

- Citronella and lemongrass. The first harvest can take place 6-9 months after planting. Then the grass can then be harvested up to four times a year. If harvested too often, the productivity of the plant will be reduced and the plant may even die. If the plant is allowed to grow too large, the oil yield is reduced. For lemongrass it should be 1.2m high with 4 - 5 leaves. The grass should be harvested early in the morning during dry periods.

- Cinnamon bark is harvested during the wet season since the rains facilitate the peeling of the bark. Harvesting involves the removal of bark from stems measuring 1.2-5 cm in diameter. This takes place early in the morning.

- Spices should be harvested correctly and at the correct stage of maturity. The main obstacle to correct harvesting is the crop being picked immature.

- Flowers such as ylang-ylang, should be picked very carefully and processed as soon as possible.

Sl. No.	Plants	Maximum final moisture content % (wet basis)
1.	Mace	10
2.	Nutmeg, cloves	9
3.	Turmeric, coriander	6
4.	Cinnamon	11-15
5.	Pepper	10 - 15
6.	Cardamom	8 - 10
7.	Ginger	15
8.	Chilli	8 - 12
9.	Pimento	12 - 15

The preparation of the material for distillation varies. Some materials, and in particular flowers, should be distilled as quickly as possible. Many herbs are left to wilt, or are dried before distillation while barks, seeds

and roots can be dried and stored for several months prior to distillation. Information on small scale drying systems can be found in the Practical Action Technical Briefs on drying. As oil may be lost during drying care needs to be taken and low temperatures used. Allowing leaves to dry in the shade or partial shade will result in less loss than direct sun drying. Leaves should never be piled high in heaps as this will not allow drying and may even encourage fermentation. It is vital that the material is dried to a moisture content that is low enough to prevent the growth of moulds.

Distillation of Oil

Distillation is a method of separating liquids in a solution by using the differences in their boiling points. It's best known for its use in distilling strong alcoholic beverages, but it also has many other commercial applications. There are specific types of distillation based on the specific mechanism used in the process.

Separation of components from a liquid mixture via distillation depends on the differences in boiling points of the individual components. Also, depending on the concentrations of the components present, the liquid mixture will have different boiling point characteristics. Therefore, distillation processes depends on the vapour pressure characteristics of liquid mixtures.

Distillation is an important commercial process that is used in the purification of a large variety of materials. For a liquid, the process involves vaporization and for a solid it is called sublimation. Both processes require heat. All substances regardless of whether they are liquids or solids are characterized by a vapour pressure. The vapour pressure of a pure substance is the pressure exerted by the substance against the external pressure which is usually atmospheric pressure. Vapour pressure is a measure of the tendency of a condensed substance to escape the condensed phase. The larger the vapor pressure, the greater the tendency to escape. When the vapor pressure of a liquid substance reaches the external pressure, the substance is observed to boil. If the external pressure is atmospheric pressure, the temperature at which a pure substance boils is called the normal boiling point. Solid substances are not characterized by a similar phenomenon as boiling. They simply vaporize directly into the atmosphere. Both vaporization and sublimation are processes that can be used to purify compounds.

Vapour pressure is an equilibrium property. At equilibrium, the process of vaporization is compensated by an equal amount of condensation. Incidentally, if vaporization is an endothermic process (i.e. heat is absorbed), condensation must be an exothermic process (i.e. heat is liberated). Now consider how vapor pressure varies with temperature. Figure 1 illustrates that vapor pressure is a very sensitive function of temperature. It does not increase linearly but in fact increases exponentially with temperature. A useful rule of thumb is that the vapor pressure of a substance roughly doubles for every increase in 10 °C. If we follow the temperature dependence of vapor pressure for a substance like water left out in an open container, we would find that the equilibrium vapor pressure of water would increase until it reached 1 atmosphere or 101325 Pa (101.3 kPa, 760 mm Hg). At this temperature and pressure, the water would begin to boil and would continue to do so until all of the water distilled or boiled off. It is not possible to achieve a vapor pressure greater than 1 atmosphere in a container left open to the atmosphere. Of course, if there is a lid on the container, the vapor pressure of water or any other substance for that matter would continue to rise with temperature until the container ruptured. Elevation of the boiling point with increase in external pressure is the principle behind it.

Steps of Distillation

Boiling

The boiling point of a pure liquid is defined as the temperature at which the vapor pressure of the liquid exactly equals the pressure exerted on it by the atmosphere and is one of its characteristic physical properties. The boiling point is used to characterize a new organic liquid, and knowledge of the boiling point is used to compare one organic liquid with another, as in the process of identifying an unknown organic substance. The boiling point of a mixture is a function of the vapor pressures of the various components in the mixture. Impurities either raise or lower the observed boiling point of a sample, depending on how the impurity interacts with the compound for which the boiling point is being measured.

The distillation of a mixture containing two different substances essentially involves heating the solution to a temperature between the two boiling points. The more-volatile substance will become a gas while the less-volatile substance will remain a liquid.

Collection

The gas of the more-volatile substance is carried away so that it can't mix in with the remaining liquid. It may then be condensed and cooled back into a separate liquid.

Considerations

A liquid does not immediately turn into a gas once its boiling point is reached. The vapor that's produced by heating the solution will actually contain both substances, although it will have a higher concentration of the more-volatile substance.

Purification

Distillation won't produce components of extremely high purity by itself. This requires chemical-separation techniques to be performed on the distilled product.

Types of Distillation

SIMPLE DISTILLATION

In simple distillation, all the hot vapors produced are immediately channeled into a condenser that cools and condenses the vapors. Therefore, the distillate will not be pure - its composition will be identical to the composition of the vapors at the given temperature and pressure, and can be computed from Raoult's law.

As a result, simple distillation is usually used only to separate liquids whose boiling points differ greatly or to separate liquids from in volatile solids or oils. For these cases, the vapor pressures of the components are usually sufficiently different that Raoult's law may be neglected due to the insignificant contribution of the less volatile component. In this case, the distillate may be sufficiently pure for its intended purpose.

1. Distillation involves 2 stages and both are physical state changes.
2. The liquid or solution mixture is boiled to vaporise the most volatile component in the mixture (liquid → gas).
3. The vapour is cooled by cold water in the condenser to condense (gas → liquid) it back to a liquid (the distillate) which is collected.
4. This can be used to purify Liquids (like water) because the dissolved solids have a much higher boiling point and will not evaporate with the steam, BUT it is too simple a method to separate a mixture of liquids especially if the boiling points are relatively close.
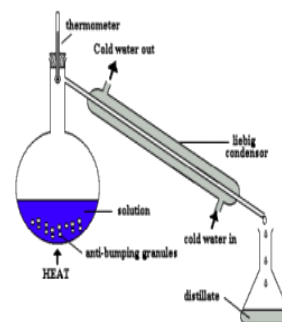
Vapour Pressure and Boiling

The vapour pressure of a liquid at a particular temperature is the equilibrium pressure exerted by molecules leaving and entering the liquid surface. Some important points regarding vapour pressure:

- Energy input raises vapour pressure
- Vapour pressure is related to boiling
- A liquid is said to 'boil' when its vapour pressure equals the surrounding pressure
- The ease with which a liquid boils depends on its volatility
- Liquids with high vapour pressures (volatile liquids) will boil at lower temperatures
- The vapour pressure and hence the boiling point of a liquid mixture depends on the relative amounts of the components in the mixture
- Distillation occurs because of the differences in the volatility of the components in the liquid mixture
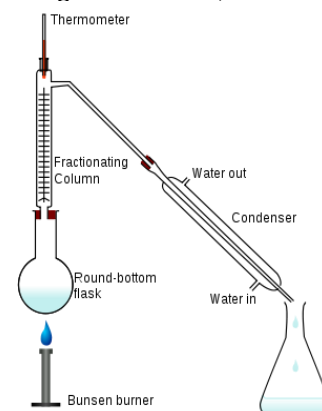
FRACTIONAL DISTILLATION

For many cases, the boiling points of the components in the mixture will be sufficiently close that Raoult's law must be taken into consideration. Therefore, fractional distillation must be used in order to separate the components well by repeated vaporization-condensation cycles within a packed fractionating column. This separation, by successive distillations, is also referred to as rectification.

As the solution to be purified is heated, its vapors rise to the fractionating column. As it rises, it cools, condensing on the condenser walls and the surfaces of the packing material. Here, the condensate continues to be heated by the rising hot vapors; it vaporizes once more. However, the compositions of the fresh vapors are determined once again by Raoult's law. Each vaporization-condensation cycle (called a theoretical plate) will yield a purer solution of the more volatile component. In reality, each cycle at a given temperature does not occur at exactly the same position in the fractionating column; theoretical plate is thus a concept rather than an accurate description.

More theoretical plates lead to better separations. A spinning band distillation system uses a spinning band of Teflon or metal to force the rising vapors into close contact with the descending condensate, increasing the number of theoretical plates.

Fractional distillation is the separation of a mixture into its component parts, or fractions, such as in separating chemical compounds by their boiling point by heating them to a temperature at which several fractions of the compound will evaporate. It is a special type of distillation. Generally the component parts boil at less than 25 °C from each other under a pressure of one atmosphere (atm). If the difference in boiling points is greater than 25 °C, a simple distillation is used.

Fractional distillation in a laboratory makes use of common laboratory glassware and apparatuses, typically including a Bunsen burner, a round-bottomed flask and a condenser, as well as the single-purpose fractionating column.

Fractional distillation uses a continuing vaporization-condensation cycle to heat the vapors in a fractionating column. This technique is used when the boiling points of the liquids are too close to be separated by simple distillation.

Fractional distillation involves 2 main stages and both are physical state changes. It can only work with liquids with different boiling points. However, this method only works if all the liquids in the mixture are miscible (e.g. alcohol/water, crude oil etc.) and do NOT separate out into layers like oil/water.

1. The liquid or solution mixture is boiled to vaporise the most volatile component in the mixture (liquid → gas). The ant-bumping granules give a smoother boiling action.

2. The vapour passes up through a fractionating column, where the separation takes place (theory at the end). This column is not used in the simple distillation described above.

3. The vapour is cooled by cold water in the condenser to condense (gas → liquid) it back to a liquid (the distillate) which is collected.

This can be used to separate alcohol from a fermented sugar solution. It is used on a large scale to separate the components of crude oil, because the different hydrocarbons have different boiling and condensation points

Apparatus

Fractional distillation apparatus using a Liebig condenser: A conical flask is used as a receiving flask. Here the distillation head and fractionating column are combined in one piece.

▪ Heat source, such as a hot plate with a bath, and ideally with a magnetic stirrer.

- Distilling flask, typically a round-bottom flask
- Receiving flask, often also a round-bottom flask
- Fractionating column
- distillation head
- thermometer and adapter if needed
- condenser, such as a Liebig condenser, Graham condenser or Allihn condenser
- vacuum adapter (not used in image to the right)
- boiling chips, also known as anti-bumping granules
- Standard laboratory glassware with ground glass joints, e.g. quickfit apparatus.

Theory of Fractional Distillation

As the vapour from the boiling mixture enters the fractionating column it begins to cool and condense. The highest boiling or least volatile liquid tends to condense more i.e. the yellow liquid (water). The lower boiling more volatile blue liquid gets further up the column. Gradually up the column the blue and yellow separate from each other so that yellow condenses back into the flask and pure blue distils over to be collected. The 1st liquid, the lowest boiling point, is called the 1st fraction and each liquid distils over when the top of the column reaches its particular boiling point to give the 2nd, 3rd fraction etc.

To increase the separation efficiency of the tall fractionating column, it is usually packed with glass beads, short glass tubes or glass rings etc. which greatly increase the surface area for evaporation and condensation.

In the distillation of crude oil the different fractions are condensed out at different points in a huge fractionating column. At the top are the very low boiling fuel gases like butane and at the bottom are the high boiling big molecules of waxes and tar.

Discussion

As an example, consider the distillation of a mixture of water and ethanol. Ethanol boils at 78.4 °C while water boils at 100 °C. So, by gently heating the mixture, the most volatile component will concentrate to a greater degree in the vapor leaving the liquid. Some mixtures form azeotropes, where the mixture boils at a lower temperature than either component. In this example, a mixture of 96% ethanol and 4% water boils at 78.2 °C, being more volatile than pure ethanol. For this reason, ethanol cannot be completely purified by direct fractional distillation of ethanol-water mixtures.

The apparatus is assembled as in the diagram. (The diagram represents a batch apparatus, as opposed to a continuous apparatus.) The mixture is put into the round bottomed flask along with a few anti-bumping granules (or a Teflon coated magnetic stirrer bar if using magnetic stirring), and the fractionating column is fitted into the top. As the mixture boils, vapor rises up the column. The vapor condenses on the glass platforms, known as trays, inside the column, and runs back down into the liquid below, refluxing distillate. The column is heated from the bottom. The efficiency in terms of the amount of heating and time required to get fractionation can be improved by insulating the outside of the column in an insulator such as wool, aluminium foil or preferably a vacuum jacket. The hottest tray is at the bottom and the coolest is at the top. At steady state conditions, the vapor and liquid on each tray are at equilibrium. Only the most volatile of the vapors stays in gaseous form all the way to the top. The vapor at the top of the column, then passes into the condenser, which cools it down until it liquefies. The separation is more pure with the addition of more trays (to a practical limitation of heat, flow, etc.) The condensate that was initially very close to the azeotrope composition becomes gradually richer in water. The process continues until all the ethanol boils out of the mixture. This point can be recognized by the sharp rise in temperature shown on the thermometer.

Typically the example above now only reflects the theoretical way fractionation works. Normal laboratory fractionation columns will be simple glass tubes (often vacuum jacketed, and sometimes internally silvered) filled with a packing, often small glass helices of 4 to 7 mm diameter. Such a column can be calibrated by the distillation of a known mixture system to quantify the column in terms of number of theoretical plates. To improve fractionation the apparatus is set up to return condensate to the column by the use of some sort of reflux splitter (reflux wire, gago, Magnetic swinging bucket, etc.) - a typical careful fractionation would employ a reflux ratio of around 10:1 (10 parts returned condensate to 1 part condensate take off).

In laboratory distillation, several types of condensers are commonly found. The Liebig condenser is simply a straight tube within a water jacket, and is the simplest (and relatively least expensive) form of condenser. The Graham condenser is a spiral tube within a water jacket, and the Allihn condenser has a series of large and small constrictions on the inside tube, each increasing the surface area upon which the vapor constituents may condense.
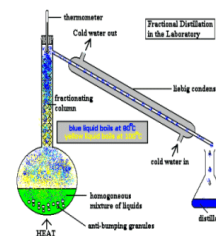
STEAM DISTILLATION

Steam distillation is a method for distilling compounds which are heat-sensitive. This process involves bubbling steam through a heated mixture of the raw material. By Raoult's law, some of the target compound will vaporize (in accordance with its partial pressure). The vapor mixture is cooled and condensed, usually yielding a layer of oil and a layer of water. Steam distillation of various aromatic herbs and flowers can result in two products; an essential oil as well as a watery herbal distillate. The essential oils are often used in perfumery and aromatherapy while the watery distillates have many applications in aromatherapy, food processing and skin care. Steam distillation is a special type of distillation (a separation process) for temperature sensitive materials like natural aromatic compounds.

Many organic compounds tend to decompose at high sustained temperatures. Separation by normal distillation would then not be an option, so water or steam is introduced into the distillation apparatus. By adding water or steam, the boiling points of the compounds are depressed, allowing them to evaporate at lower temperatures, preferably below the temperatures at which the deterioration of the material becomes appreciable. If the substances to be distilled are very sensitive to heat, steam distillation can also be combined with vacuum distillation. After distillation the vapors are condensed as usual, usually yielding a two-phase system of water and the organic compounds, allowing for simple separation.

Principle

When a mixture of two practically immiscible liquids is heated while being agitated to expose the surfaces of both the liquids to the vapor phase, each constituent independently exerts its own vapor pressure as a function of temperature as if the other constituent were not present. Consequently, the vapor pressure of the whole system increases. Boiling begins when the sum of the partial pressures of the two immiscible liquids just exceeds the atmospheric pressure (approximately 101 kPa at sea level). In this way, many organic compounds insoluble in water can be purified at a temperature well below the point at which decomposition occurs. For example, the boiling point of bromobenzene is 156 °C and the boiling point of water is 100 °C, but a mixture of the two boils at 95 °C. Thus, bromobenzene can be easily distilled at a temperature 61 C° below its normal boiling point.

Applications

Steam distillation is employed in the manufacture of essential oils, for instance, perfumes. In this method, steam is passed through the plant material containing the desired oils. It is also employed in the synthetic procedures of complex organic compounds. Eucalyptus oil and orange oil are obtained by this method on the industrial scale. Steam distillation is also widely used in petroleum refineries and petrochemical plants where it is commonly referred to as steam stripping. Other industrial uses of steam distillation include the production of consumer food products such as sprayable or aerosolized condiments such as sprayable mayonnaise.

How Does an Essential Oil Distiller Work?

Setting up the Diffuser

The distiller is set up so that the plant or herb that is being used to create the essential oil is placed in a container that allows steam to enter and to escape. Water is added to a container on one side of the plant container and connected to the bottom of it via a tube of some kind. A second container of cold water is placed on the other side of the plants and connected to the top of it via a hose.

Creating Steam

Water in the first container is exposed to a heat source. As the water heats up, it becomes steam and escapes from the container through the hose that is connected. The steam travels through the hose into the chamber holding the plants.

Releasing the Essential Oil

As the steam rises through the container holding the plants, it causes the oil membranes to open, releasing the essential oils. This process prevents the membrane that surrounds the oil from bursting, which ruins the oil. The oil evaporates and is taken with the steam up through the tube attached at the top of the container.

Condensing the Steam

The steam containing oil and water is taken to a container containing cool water. The water cools the steam, causing it to condense into liquid. The oil is taken with the steam into a water cooler. As the steam cools, it condenses and becomes a liquid again.

Collecting the Essential Oil

The extracted oil sits on top of the water, allowing it to be easily collected by skimming it off the top. The essential oil can then be used for its intended purpose. The leftover water has some soothing properties because it retains some of the aroma of the oil.

WATER DISTILLATION

Water distillation is the simplest and cheapest distillation method. The plant material is totally immersed in water and boiled. The steam and oil vapour is condensed and the oil is separated from the water using the system. The stills used are simple and suitable for smallholder farmers. They are often heated over an open fire, which if not carefully controlled, may result in local overheating and burning of the charge. The quality of the oils produced in such traditional stills can be improved if they are heated by steam generated in a separate boiler. This, however, requires more expenditure in capital equipment. Water distillation remains the recommended method for barks, such as cinnamon and sandlewood, and certain flowers.

WATER-STEAM DISTILLATION

Water-steam distillation is an improvement of simple water distillation. The charge of plant material is supported on a mesh or grill above boiling water. The water is boiled, either over a fire or by steam from a boiler using a steam coil or jacket. This system greatly reduces local overheating and burning of the charge. It is important that the charge is packed evenly and not too tightly into the still. Over-packing will result in back-pressure and the steam finding channels through the charge leaving zones that have not been extracted.

Steam distillation

Steam distillation is the most advanced method and depends on live steam being supplied from an external boiler. The charge is again supported on a mesh above the base of the still and above a steam coil. The principle advantage of this method is that "dry steam" is used which results in reduced distillation times and hence greater outputs.

All still bodies should be insulated to reduce heat losses and fuel consumption. In some cases they are mounted on frames that allow them to be inverted in order to rapidly remove the hot charge after distillation. This reduces "turn round times" and increases daily outputs.

Modern still bodies are usually made from stainless steel while traditional systems use mild steel. For the reasons described below, in many cases, the use of expensive stainless steel is not necessary.

Condensers

Steam containing the essential oil vapour leaves the still via a head, known as a gooseneck, and passes to a condenser. Simple condensers consist of a metal coil in a tank of flowing cold water. Ideally the coil of the condenser should be constructed from an inert material such as stainless steel in order to prevent the oil chemically reacting with mild steel. In many traditional stills the gooseneck and condenser coil were constructed from copper or brass that had been internally tinned to provide a reasonably inert surface. It is very important that the condensed steam (water) leaving the condenser is thoroughly cooled. If it is still warm there will be a loss of essential oil.

Oil Separation

The final step in the distillation of essential oils is the separation from the water flowing from the condenser using a special flask called a Florentine. This is a very important stage as small quantities of oils of very high value are being handled and maximum efficiency is the key to profitability.

Most essential oils are lighter than water and float to the surface of the Florentine. Some oils, however, are denser than water and sink to the bottom. For this reason two types of Florentine are used. It is common practice to link several Florentines together. Most of the oil will separate in the first flask but some will pass over with the water to the subsequent Florentine flask. To determine whether the oil is lighter or heavier than water, the mixture is allowed to settle in a glass container. If the oil is heavier than water, the oil is collected from the bottom of the container, and if lighter from the top. If the water is cloudy after separation, it should be returned to the distillation unit and redistilled. This is called 'cohabitation'.

At the end of the distillation the oil and water in the Florentines is placed in a large laboratory separating funnel and allowed stand for several hours after which the water can be run off. At is stage a small plug of cotton wool is often placed in the outlet of the funnel. As the oil runs through the plug any final traces of water are removed by the cotton wool.

The oil should be stored in brown glass bottles or drums, tightly closed and with the minimum possible headspace as oxygen in the air reacts with many oils and can alter their fragrant characteristics.

INDUSTRIAL DISTILLATION

Distillation is the most common form of separation technology used in petroleum refineries, petrochemical and chemical plants, natural gas processing and cryogenic air separation plants. In most cases, the distillation is operated at a continuous steady state. New feed is always being added to the distillation column and products are always being removed. Unless the process is disturbed due to changes in feed, heat, ambient temperature, or condensing, the amount of feed being added and the amount of product being removed are normally equal. This is known as continuous, steady-state fractional distillation.

Industrial distillation is typically performed in large, vertical cylindrical columns known as distillation or fractionation towers or distillation columns with diameters ranging from about 65 centimetres to 6 metres and heights ranging from about 6 m X 60 m or more. The distillation towers have liquid outlets at intervals up the column which allow for the withdrawal of different fractions or products having different boiling points or boiling ranges.

By increasing the temperature of the product inside the columns, the different hydrocarbons are separated. The lightest products (those with the lowest boiling point) exit from the top of the columns and the heaviest products (those with the highest boiling point) exit from the bottom of the column.

For example, fractional distillation is used in oil refineries to separate crude oil into useful substances (or fractions) having different hydrocarbons of different boiling points. The crude oil fractions with higher boiling points:

- have more carbon atoms
- have higher molecular weights
- are more branched chain alkanes

- are darker in color
- are more viscous
- are more difficult to ignite and to burn

Large scale industrial distillation applications include both batch and continuous fractional, vacuum, azeotropic, extractive and steam distillation.Industrial distillation is typically performed in large, vertical cylindrical columns known as distillation towers or distillation columns with diameters ranging from about 65 centimeters to 16 meters and heights ranging from about 6 meters to 90 meters or more. When the process feed has a diverse composition, as in distilling crude oil, liquid outlets at intervals up the column allow for the withdrawal of different fractions or products having different boiling points or boiling ranges. The lightest products (those with the lowest boiling point) exit from the top of the columns and the heaviest products (those with the highest boiling point) exit from the bottom of the column and are often called the bottoms.

Industrial towers use reflux to achieve a more complete separation of products. Reflux refers to the portion of the condensed overhead liquid product from a distillation or fractionation tower that is returned to the upper part of the tower as shown in the schematic diagram of a typical, large-scale industrial distillation tower. Inside the tower, the downflowing reflux liquid provides cooling and condensation of the upflowing vapors thereby increasing the efficiency of the distillation tower. The more reflux that is provided for a given number of theoretical plates, the better the tower's separation of lower boiling materials from higher boiling materials. Alternatively, the more reflux that is provided for a given desired separation, the fewer the number of theoretical plates required.

Such industrial fractionating towers are also used in air separation, producing liquid oxygen, liquid nitrogen, and high purity argon. Distillation of Chlorosilanes also enables the production of high-purity silicon for use as a semiconductor.

Design and operation of a distillation tower depends on the feed and desired products. Given a simple, binary component feed, analytical methods such as the McCabe-Thiele method or the Fenske equation can be used. For a multi-component feed, simulation models are used both for design and operation. Moreover, the efficiencies of the vapor-liquid contact devices (referred to as plates or trays) used in distillation towers are typically lower than that of a theoretical 100% efficient equilibrium stage. Hence, a distillation tower needs more trays than the number of theoretical vapor-liquid equilibrium stages.

In modern industrial uses, generally a packing material is used in the column instead of trays, especially when low pressure drops across the column are required, as when operating under vacuum.

This packing material can either be random dumped packing (1-3" wide) such as Raschig rings or structured sheet metal. Liquids tend to wet the surface of the packing and the vapors pass across this wetted surface, where mass transfer takes place. Unlike conventional tray distillation in which every tray represents a separate point of vapor-liquid equilibrium, the vapor-liquid equilibrium curve in a packed column is continuous. However, when modeling packed columns, it is useful to compute a number of theoretical stages to denote the separation efficiency of the packed column with respect to more traditional trays. Differently shaped packings have different surface areas and void space between packings. Both of these factors affect packing performance.

Another factor in addition to the packing shape and surface area that affects the performance of random or structured packing is the liquid and vapor distribution entering the packed bed. The number of theoretical stages required to make a given separation is calculated using a specific vapor to liquid ratio. If the liquid and vapor are not evenly distributed across the superficial tower area as it enters the packed bed, the liquid to vapor ratio will not be correct in the packed bed and the required separation will not be achieved. The packing will appear to not be working properly. The height equivalent of a theoretical plate (HETP) will be greater than expected. The problem is not the packing itself but the mal-distribution of the fluids entering the packed bed. Liquid mal-distribution is more frequently the problem than vapor. The design of the liquid distributors used to introduce the feed and reflux to a packed bed is critical to making the packing perform to it maximum efficiency. Methods of evaluating the effectiveness of a liquid distributor to evenly distribute the liquid entering a packed bed can be found in references.

Large-scale industrial towers use reflux to achieve a more complete separation of products. Reflux refers to the portion of the condensed overhead liquid product from a distillation or fractionation tower that is returned to the upper part of the tower as shown in the schematic diagram of a typical, large-scale industrial distillation tower. Inside the tower, the reflux liquid flowing downwards provides the cooling needed to condense the vapors flowing upwards, thereby increasing the effectiveness of the distillation tower.

The more reflux is provided for a given number of theoretical plates, the better the tower's separation of lower boiling materials from higher boiling materials. Alternatively, the more reflux provided for a given desired separation, the fewer theoretical plates are required.

Crude oil is separated into fractions by fractional distillation. The fractions at the top of the fractionating column have lower boiling points than the fractions at the bottom. The heavy bottom fractions are often cracked into lighter, more useful products. All of the fractions are processed further in other refining units

Fractional distillation is also used in air separation, producing liquid oxygen, liquid nitrogen, and highly concentrated argon. Distillation of chlorosilanes also enables the production of high-purity silicon for use as a semiconductor.

In industrial uses, sometimes a packing material is used in the column instead of trays, especially when low pressure drops across the column are required, as when operating under vacuum. This packing material can either be random dumped packing (1-3" wide) such as Raschig rings or structured sheet metal. Typical manufacturers are Koch, Sulzer and other companies. Liquids tend to wet the surface of the packing and the vapors pass across this wetted surface, where mass transfer takes place. Unlike conventional tray distillation in which every tray represents a separate point of vapor liquid equilibrium the vapor liquid equilibrium curve in a packed column is continuous. However, when modeling packed columns it is useful to compute a number of "theoretical plates" to denote the separation efficiency of the packed column with respect to more traditional trays. Differently shaped packings have different surface areas and void space between packings. Both of these factors affect packing performance.

## Design of industrial distillation columns

Design and operation of a distillation column depends on the feed and desired products. Given a simple, binary component feed, analytical methods such as the McCabe-Thiele method or the Fenske equation can be used. For a multi-component feed, simulation models are used both for design and operation.

Moreover, the efficiencies of the vapor-liquid contact devices (referred to as *plates* or *trays*) used in distillation columns, are typically lower than that of a theoretical 100% efficient equilibrium stage. Hence, a distillation column needs more plates than the number of theoretical vapor-liquid equilibrium stages.

An indication of numbers: the separation of two compounds with relative volatility of 1.1 requires a minimum of 130 theoretical plates with a minimum reflux ratio of 20.. With a relative volatility of 4, the required number of theoretical plates decreased to 9 with a reflux ratio of 0.66. In another source, a boiling point difference of 30 °C requires 12 theoretical plates and, for a difference of 3 °C, the number of plates increased to 1000.

The reflux ratio is the ratio of the amount of moles returned as refluxed liquid to the fractionating column and the amount of moles of final product, both per unit time.

Continuous distillation, a form of distillation, is an ongoing separation in which a mixture is continuously (without interruption) fed into the process and separated fractions are removed continuously as output streams. A distillation is the separation or partial separation of a liquid feed mixture into components or fractions by selective boiling (or evaporation) and condensation. A distillation produces at least two output fractions. These
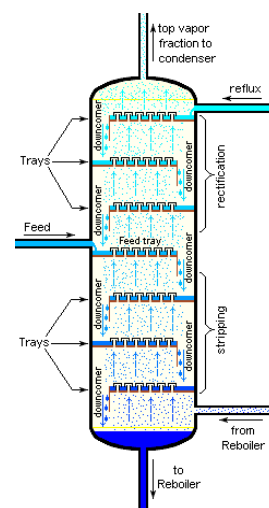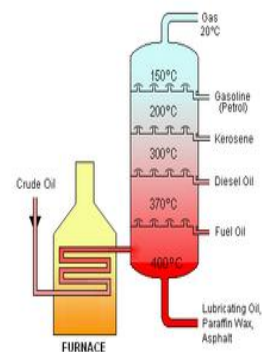
fractions include at least one volatile distillate fraction, which has boiled and been separately captured as a vapor condensed to a liquid, and practically always a bottoms (or residuum) fraction, which is the least volatile residue that has not been separately captured as a condensed vapor.

An alternative to continuous distillation is batch distillation, where the mixture is added to the unit at the start of the distillation, distillate fractions are taken out sequentially in time (one after another) during the distillation, and the remaining bottoms fraction is removed at the end. Because each of the distillate fractions are taken out at different times, only one distillate exit point (location) is needed for a batch distillation and the distillate can just be switched to a different receiver, a fraction-collecting container. Batch distillation is often used when smaller quantities are distilled. In a continuous distillation, each of the fraction streams is taken simultaneously throughout operation; therefore, a separate exit point is needed for each fraction. In practice when there are multiple distillate fractions, each of the distillate exit points are located at different heights on a fractionating column. The bottoms fraction can be taken from the bottom of the distillation column or unit, but is often taken from a re boiler connected to the bottom of the column.

Each fraction may contain one or more components (types of chemical compounds). When distilling crude oil or a similar feedstock, each fraction contains many components of similar volatility and other properties. Although it is possible to run a small-scale or laboratory continuous distillation, most often continuous distillation is used in a large-scale industrial process.

Batch distillation refers to the use of distillation in batches, meaning that a mixture is distilled to separate it into its component fractions before the distillation still is again charged with more mixture and the process is repeated. This is in contrast with continuous distillation where the feedstock is added and the distillate drawn off without interruption. Batch distillation has always been an important part of the production of seasonal, or low capacity and high-purity chemicals. It is a very frequent separation process in the pharmaceutical industry and in wastewater treatment units.

Molecular Distillation

Molecular distillation is vacuum distillation below the pressure of 0.01 torr. 0.01 torr is one order of magnitude above high vacuum, where fluids are in the free molecular flow regime, i.e. the mean free path of molecules is comparable to the size of the equipment. The gaseous phase no longer exerts significant pressure on the substance to be evaporated, and consequently, rate of evaporation no longer depends on pressure. That is, because the continuum assumptions of fluid dynamics no longer apply, mass transport is governed by molecular dynamics rather than fluid dynamics. Thus, a short path between the hot surface and the cold surface is necessary, typically by suspending a hot plate covered with a film of feed next to a cold plate with a line of sight in between. Molecular distillation is used industrially for purification of oils.

Vacuum Distillation

Some compounds have very high boiling points. To boil such compounds, it is often better to lower the pressure at which such compounds are boiled instead of increasing the temperature. Once the pressure is lowered to the vapor pressure of the compound (at the given temperature), boiling and the rest of the distillation process can commence. This technique is referred to as vacuum distillation and it is commonly found in the laboratory in the form of the rotary evaporator. This technique is also very useful for compounds which boil beyond their decomposition temperature at atmospheric pressure and which would therefore be decomposed by any attempt to boil them under atmospheric pressure.

Vacuum distillation is a method of distillation whereby the pressure above the liquid mixture to be distilled is reduced to less than its vapor pressure (usually less than atmospheric pressure) causing evaporation of the most volatile liquid(s) (those with the lowest boiling points). This distillation method works on the principle that boiling occurs when the vapor pressure of a liquid exceeds the ambient pressure. Vacuum distillation is used with or without heating the solution.

Laboratory Scale Applications

Laboratory-scale vacuum distillation is used when liquids to be distilled have high atmospheric boiling points or chemically change at temperatures near their atmospheric boiling points. Temperature sensitive

materials (such as beta carotene) also require vacuum distillation to remove solvents from the mixture without damaging the product. Another reason vacuum distillation is used is that compared to steam distillation there is a lower level of residue build up. This is important in commercial applications where temperature transfer is produced using heat exchangers.

Vacuum distillation is sometimes referred to as low temperature distillation. Temperature sensitive materials (such as beta carotene) also require vacuum distillation to remove solvents from the mixture without damaging the product. There many laboratory applications for vacuum distillation as well as many types of distillation set-ups and apparatuses.

Safety is an important consideration when using glassware as part of the set-up. All of the glass components should be carefully examined for scratches and cracks which could result in implosions when the vacuum is applied. Wrapping as much of the glassware with tape as is practical helps to prevent dangerous scattering of glass shards in the event of an implosion.

Rotary Evaporation

Rotary evaporation is a type of vacuum distillation apparatus used to remove bulk solvents from the liquid being distilled. It is also used by environmental regulatory agencies for determining the amount of solvents in paint, coatings and inks.

Rotary evaporation set-ups include an apparatus referred to as a *Rotovap* which rotates the distillation flask (sometimes called the *still pot*) to enhance the distillation. Rotating the flask throws up liquid on the walls of the flask and thus increases the surface area for evaporation. Heat is often applied to the rotating distillation flask by partially immersing it in a heated bath of water or oil. Typically, the vacuum in such systems is generated by a water aspirator or a vacuum pump of some type.

Distillation of High-boiling and/or air sensitive materials

Some compounds have high boiling point temperatures as well as being air sensitive. A simple laboratory vacuum distillation glassware set-up can be used, in which the vacuum can be replaced with an inert gas after the distillation is complete.
However, this is not a completely satisfactory system if it is desired to collect fractions under a reduced pressure. For better results or for very air sensitive compounds, either a Perkin triangle distillation set-up or a short-path distillation set-up can be used.

Perkin triangle distillation set-up

The Perkin triangle set-up uses a series of Teflon valves to allow the distilled fractions to be isolated from the distillation flask without the main body of the distillation set-up being removed from either the vacuum or the heat source, and thus can remain in a state of reflux.
To do this, the distillate receiver vessel is first isolated from the vacuum by means of the Teflon valves.

The vacuum over the sample is then replaced with an inert gas (such as nitrogen or argon) and the distillate receiver can then be stoppered and removed from the system.

Vacuum distillation set-up using a short-path head

Vacuum distillation of moderately air/water-sensitive liquid can be done using standard Schlenk-line techniques. When assembling the set-up apparatus, all of the connecting lines are clamped so that they cannot pop off.

Once the apparatus is assembled, and the liquid to be distilled is in the still pot, the desired vacuum is established in the system by using the vacuum connection on the short-path distillation head. Care is taken to prevent potential bumping as the liquid in the still pot degases.

While establishing the vacuum, the flow of coolant is started through the short-path distillation head. Once the desired vacuum is established, heat is applied to the still pot.

If needed, the first portion of distillate can be discarded by purging with inert gas and changing out the distillate receiver.

When the distillation is complete: the heat is removed, the vacuum connection is closed, and inert gas is purged through the distillation head and the distillate receiver. While under the inert gas purge, remove the distillate receiver and cap it with an air-tight cap. The distillate receiver can be stored under vacuum or under inert gas by using the side-arm on the distillation flask.

Industrial-Scale Applications

Large-scale Vacuum Distillation Towers

Typical industrial applications utilize the heat pump cycle to maximize efficiency. This type of distillation is in use in the oil industry where common ASTM standards are D1160, D2892, D 5236. These standards describe typical applications of vacuum distillation at pressures of about 1-100 mbar. Pilot plants up to 60 L can be built in accordance with these standards.

Industrial-scale vacuum distillation has several advantages. Close boiling mixtures may require many equilibrium stages to separate the key components. One tool to reduce the number of stages needed is to utilize vacuum distillation. Vacuum distillation columns (as depicted in the drawing to the right) typically used in oil refineries have diameters ranging up to about 14 metres (46 feet), heights ranging up to about 50 metres (164 feet), and feed rates ranging up to about 25,400 cubic metres per day (160,000 barrels per day).

Vacuum distillation increases the relative volatility of the key components in many applications. The higher the relative volatility, the more separable are the two components; this connotes fewer stages in a distillation column in order to effect the same separation between the overhead and bottoms products. Lower pressures increase relative volatilities in most systems.

A second advantage of vacuum distillation is the reduced temperature requirement at lower pressures. For many systems, the products degrade or polymerize at elevated temperatures.
Vacuum distillation can improve a separation by:

- Prevention of product degradation or polymer formation because of reduced pressure leading to lower tower bottoms temperatures,
- Reduction of product degradation or polymer formation because of reduced mean residence time especially in columns using packing rather than trays.
- Increasing capacity, yield, and purity.

Another advantage of vacuum distillation is the reduced capital cost, at the expense of slightly more operating cost. Utilizing vacuum distillation can reduce the height and diameter, and thus the capital cost of a distillation column.

Air-sensitive vacuum distillation

Air-sensitive vacuum distillation is similar to vacuum distillation except that it replaces the air with an inert gas instead of a vacuum. This method is used when the components are reactive with air.

Some compounds have high boiling points as well as being air sensitive. A simple vacuum distillation system as exemplified above can be used, whereby the vacuum is replaced with an inert gas after the distillation is complete. However, this is a less satisfactory system if one desires to collect fractions under a reduced pressure. To do this a "pig" adaptor can be added to the end of the condenser, or for better results or for very air sensitive compounds a Perkin triangle apparatus can be used.

The Perkin triangle, has means via a series of glass or Teflon taps to allows fractions to be isolated from the rest of the still, without the main body of the distillation being removed from either the vacuum or heat source, and thus can remain in a state of reflux. To do this, the sample is first isolated from the vacuum by means of the taps, the vacuum over the sample is then replaced with an inert gas (such as nitrogen or argon) and can then be stoppered and removed. A fresh collection vessel can then be added to the system, evacuated

and linked back into the distillation system via the taps to collect a second fraction, and so on, until all fractions have been collected.

Short path distillation

Short path distillation is a distillation technique that involves the distillate travelling a short distance, often only a few centimeters, and is normally done at reduced pressure. A classic example would be a distillation involving the distillate travelling from one glass bulb to another, without the need for a condenser separating the two chambers. This technique is often used for compounds which are unstable at high temperatures or to purify small amounts of compound. The advantage is that the heating temperature can be considerably lower (at reduced pressure) than the boiling point of the liquid at standard pressure, and the distillate only has to travel a short distance before condensing. A short path ensures that little compound is lost on the sides of the apparatus. The Kugelrohr is a kind of a short path distillation apparatus which often contain multiple chambers to collect distillate fractions.

Other types

- The process of reactive distillation involves using the reaction vessel as the still. In this process, the product is usually significantly lower-boiling than its reactants. As the product is formed from the reactants, it is vaporized and removed from the reaction mixture. This technique is an example of a continuous vs. a batch process; advantages include less downtime to charge the reaction vessel with starting material, and less workup.
- Pervaporation is a method for the separation of mixtures of liquids by partial vaporization through a non-porous membrane.
- Extractive distillation is defined as distillation in the presence of a miscible, high boiling, relatively non-volatile component, the solvent, that forms no azeotrope with the other components in the mixture.
- Flash evaporation (or partial evaporation) is the partial vaporization that occurs when a saturated liquid stream undergoes a reduction in pressure by passing through a throttling valve or other throttling device. This process is one of the simplest unit operations, being equivalent to a distillation with only one equilibrium stage.
- Codistillation is distillation which is performed on mixtures in which the two compounds are not miscible.

The unit process of evaporation may also be called "distillation":

- In rotary evaporation a vacuum distillation apparatus is used to remove bulk solvents from a sample. Typically the vacuum is generated by a water aspirator or a membrane pump.
- In a kugelrohr a short path distillation apparatus is typically used (generally in combination with a (high) vacuum) to distill high boiling (> 300 °C) compounds. The apparatus consists of an oven in which the compound to be distilled is placed, a receiving portion which is outside of the oven, and a means of rotating the sample. The vacuum is normally generated by using a high vacuum pump.

Other uses:

- Dry distillation or destructive distillation, despite the name, is not truly distillation, but rather a chemical reaction known as pyrolysis in which solid substances are heated in an inert or reducing atmosphere and any volatile fractions, containing high-boiling liquids and products of pyrolysis, are collected. The destructive distillation of wood to give methanol is the root of its common name - *wood alcohol*.
- Freeze distillation is an analogous method of purification using freezing instead of evaporation. It is not truly distillation, but a recrystallization where the product is the mother liquor, and does not produce products equivalent to distillation. This process is used in the production of ice beer and ice wine to increase ethanol and sugar content, respectively. It is also used to produce applejack. Unlike distillation, freeze distillation concentrates poisonous congeners rather than removing them.

Azeotropes

A mixture of two liquid substances almost always forms an azeotrope, meaning that the resulting mixture will have a single boiling point that's between the boiling point of the two pure substances.

Azeotropic Distillation

Interactions between the components of the solution create properties unique to the solution, as most processes entail nonideal mixtures, where Raoult's law does not hold. Such interactions can result in a constant-boiling azeotrope which behaves as if it were a pure compound (i.e., boils at a single temperature instead of a range). At an azeotrope, the solution contains the given component in the same proportion as the vapor, so that evaporation does not change the purity, and distillation does not effect separation. For example, ethyl alcoholand water forms an azeotrope of 95.6% at 78.1 °C.

If the azeotrope is not considered sufficiently pure for use, there exist some techniques to break the azeotrope to give a pure distillate. This set of techniques is known as azeotropic distillation. Some techniques achieve this by jumping over the azeotropic composition (by adding an additional component to create a new azeotrope, or by varying the pressure). Others work by chemically or physically removing or sequestering the impurity. For example, to purify ethanol beyond 95%, a drying agent or a (desiccant such as potassium carbonate) can be added to convert the soluble water into insoluble water of crystallization. Molecular sieves are often used for this purpose as well.

Immiscible liquids, such as water and toluene, easily form azeotropes. Commonly, these azeotropes are referred to as a low boiling azeotrope because the boiling point of the azeotrope is lower than the boiling point of either pure component. The temperature and composition of the azeotrope is easily predicted from the vapor pressure of the pure components, without use of Raoult's law. The azeotrope is easily broken in a distillation set-up by using a liquid-liquid separator (a decanter) to separate the two liquid layers that are condensed overhead. Only one of the two liquid layers is refluxed to the distillation set-up.

High boiling azeotropes, such as a 20 weight percent mixture of hydrochloric acid in water, also exist. As implied by the name, the boiling point of the azeotrope is greater than the boiling point of either pure component.

To break azeotropic distillations and cross distillation boundaries, such as in the DeRosier Problem, it is necessary to increase the composition of the light key in the distillate.

In chemistry, azeotropic distillation is any of a range of techniques used to break an azoetrope in distillation. In chemical engineering, *azeotropic distillation* usually refers to the specific technique of adding another component to generate a new, lower-boiling azeotrope that is heterogeneous (e.g. producing two, immiscible liquid phases), such as the example below with the addition of benzene to water and ethanol. This practice of adding an entrainer which forms a separate phase is a specific sub-set of (industrial) azeotropic distillation methods, or combination thereof. In some senses, adding an entrainer is similar to extractive distillation.

Pressure Swing Distillation

Another method, pressure-swing distillation, relies on the fact that an azeotrope is pressure dependent. An azeotrope is not a range of concentrations that cannot be distilled, but the point at which the activity coefficients of the distillates are crossing one another. If the azeotrope can be jumped over, distillation can continue, although because the activity coefficients have crossed, the water will boil out of the remaining ethanol, rather than the ethanol out of the water as at lower concentrations.

To jump the azeotrope, the azeotrope can be moved by altering the pressure. Typically, pressure will be set such that the azeotrope will be closer to 100% concentration. For ethanol, that may be 97%. Ethanol can now be distilled up to 97%. It will actually be distilled to something slightly less, like 96.5%. The 96.5% alcohol is then sent to a distillation column that is under a different pressure, one that pulls the azeotrope down, maybe to 96%. Since the mixture is already above the 96% azeotrope, the distillation will not get "stuck" at that point and the ethanol can be distilled to whatever concentration is needed.

Pressure-swing distillation is essentially the same as the unidirectional distillation used to break azeotropic mixtures, but here both positive and negative pressures may be employed.

This has an important impact on the selectivity of the distillation and allows a chemist[J] to optimize a process such that fewer extremes of pressure and temperature are required and less energy is consumed. This is particularly important in commercial applications.

Pressure-swing distillation is employed during the industrial purification of ethyl acetate after its catalytic synthesis from ethanol.

Molecular Sieves

For the distillation of ethanol for gasoline addition, the most common means of breaking the azeotrope is the use of molecular sieves. Ethanol is distilled to 96%, then run over a molecular sieve which adsorbs water from the mixture. The concentration is now above 96% and can be further distilled. The sieve is heated to remove the water and reused.

Alternatively, if positive pressures are required, standard glassware can not be used, energy must be used for pressurization and there is a higher chance of side reactions occurring in the distillation, such as decomposition, due to the higher temperatures required to effect boiling.

A unidirectional distillation will rely on a pressure change in one direction, either positive or negative.

Solvent and enzyme extraction of essential oils

Steam distillation of essential oils uses high temperature. Many of the constituents of fragrances are liable to be modified in character as a result of such high temperature extraction. Lower-temperature extraction methods offer possibilities for improving yields and producing oils with fragrances closer to the fresh source. Sometimes a special solvent is used to extract the fragrance from such delicate flowers as jasmine. Enzymes are gaining favour in the citrus peel essential oil industry whereby the source material is reduced to a pulp, a specific enzyme is added and the mixture then extracted with a suitable solvent.

Supercritical CO$_2$ [scCO$_2$] Extraction

In recent times, developed and developing world have a strong demand for creation of healthy and less polluted environment using clean technologies and producing solvent residue free nutritional and healthcare products. These products must possess natural colour, taste and self-live extensive properties as well as must contain biologically active, health protective compounds. Supercritical fluid extraction is one of the desirable technologies, which uses carbon dioxide for extraction of essential oils, fatty oils, pigments and natural waxes from natural sources, mainly from herbs, spices and medicinal plants. According to the physicochemical properties of supercritical CO$_2$, the extraction is carried out at moderate temperature (mainly between 31-60°C), therefore thermo-labile compounds can be obtained without any decomposition. The extract is absolutely solvent residual free as the CO$_2$ is in gaseous state at room temperature. Mainly non-polar compounds can be extracted and/or fractionated as the solvating power of supercritical CO$_2$ changes within wide ranges with changes of the pressure and temperature during extraction. The extraction is carried out at relatively high pressure; therefore the investment cost of such a plant is higher than that of the conventional units, although the process is easily controlled with low operating costs.

Extraction of a number of plants including medicinal, aromatic and food species with supercritical CO$_2$ has been attempted and quality and bioactivity of isolated products have been studied by various researchers. The results support the notion that extracts obtained by supercritical CO$_2$ extraction may have roles as preservatives, natural antioxidants, colorants and flavour components in food and cosmetic systems. The effects of extraction parameters (temperature and pressure) on yields and compositions have been examined to optimize the technology.

Extraction of Thyme (*Thymus vulgaris* L.) with scCO$_2$ resulted in strongly scented brownish-green waxy extract with higher yield than that of *n*-hexane extraction. Due to the bigger characteristic particle size of thyme higher amount of scCO2 solvent is needed for overall extraction. The microbial properties of thyme essential oil obtained by scCO2 extraction showed the strongest inhibition against fungi *T. viride, A. niger*, and *P. cyclopium* and bacteria *E. coli, P. fluorescence* and *B. cereus.*

The scCO2 extraction has the potential in large-scale production of phyto-products through clean technology. The products so obtained possess high biological values; therefore the usage is reasonable for well-

defined purposes (food, cosmetic or pharmaceutical industries). Natural oils, waxes, colours, aromas and flavours can be extracted and due to their antimicrobial and antioxidant properties longer shelf-live can be achieved.

Estimation of Essential Oil by Clevenger apparatus

Clevenger apparatus is used for the determination of percentage of volatile oils present in the oil-bearing material. Take weighed quantity of material in a sample flask and add water. Generally the ratio of the material to water is 1:8. Connect the flask with Clevenger apparatus and open the tap of water for running the flow of water in a condenser. Start heating on a heating mantle and control the heat so that oil with water vapors comes into the graduated distillate receiving tube and excess water goes back into the flask. Continue heating for 8 hours, cool the assembly and remove the water from the distillate receiving tube, and take the oil into the rotary evaporator for removing the traces of water and cool the flask in a desiccators. After cooling, weight it accurately and calculate as follows:

Oil % =
$$\frac{\textit{Weight of the oil} \times 100}{\textit{Weight of the material taken}}$$

Solvent extraction of fragrant raw material

Materials used for the solvent extraction are usually powdered where as fresh plants can be homogenized. Put the weighed quantity of the sample in a thimble and cover the material with a piece of cotton so that no portion of the sample escapes out of the thimble. Then place this thimble in an extractor, which is linked with solvent flask at the bottom through two tubes. One of the tubes is a side tube for the passage of solvent vapors and the other is a siphon tube for siphoning of the extract back to the flask of the soxhlet apparatus. Fill the flask with petroleum ether of 60^0-80^0C B.P. to more than half of the flask. Fit the assembly with condenser as shown in fig.2a and start heating on a heating on a heating mantle controlling the heat so that the solvent from the condenser drops at the centre of the thimble. Continue the extraction for 4 hours, cool the contents and disconnect the flask taking out all the solvent of the thimble into the flask. Transfer the solvent into the evaporating flask of the rotary evaporator. Rotary evaporator is used for distilling off the solvent generally under vacuum. After removal of the solvent, cool the flask in a desiccator. After cooling weight it accurately and calculate as follows.

Concrete Oil %=
$$\frac{\textit{Weight of the oil} \times 10}{\textit{Weight of the material taken}}$$

Physicochemical Traits of Essential oil

Specific gravity

The specific gravity of oil is the ratio of the weights of given volume of oil at 27^0C to that of equal volume of distilled water at27^0C, all weighting being done in absence of air. The quantity is dimensionless and expressed as d27/27. This physical property is an important criterion for quality and purity of an essential oil. For determining the specific gravity accuracy to at least the third decimal place is necessary.

Apparatus

A specific gravity bottle or pyknometer is used as the most convenient and rapid method for determining the specific gravity. A conical shaped pyknometer of 5ml. capacity with a ground in thermometer and a capillary side tube with a ground cap is used.

Calculation
Specific gravity d27/27 is given by the following formula:

D27/27 =
$$\frac{M_3 -}{M_1}$$
$$M_2 - M_1$$

M1 = mass is gm .of the empty pyknometer.
M2 = mass in gm. of the pyknometer filled with water at 27^0C.
M3 = mass in gm. of the pyknometer filled with oil under test at 27^0C.

Solubility in Alcohol

Most of the essential oils are soluble in alcohol and dilute alcohol. So solubility of a particular essential oil in a specific dilute alcohol at specific temperature may be the criteria for determining its purity. Therefore, it is possible to define the solubility in alcohol as the number of volumes of dilute alcohol required for the complete solubility of one volume of oil. The determination of such solubility is a convenient and rapid test in the evaluation of the quality of oil in general. Oils rich in oxygenated constituents are more readily soluble in dilute alcohol than oils rich in terpenes (However the oxygenated constituents belonging to the sesquiterpenes series are relatively insoluble e.g. cedrol, santalol). Adulteration with relatively insoluble material will greatly affect the solubility. The solubility of oil may change with age. Polymerisation is usually accompanied with a decrease in solubility i.e. a stronger alcohol may be required to yield a clear solution. Improper storage may hasten polymerization and factors such as light, heat, air and the presence of alcohols of various strengths like 50%, 60%, 70%, 80%, 90% are customarily used in determining solubility of essential oils. Factors such as light, air, heat and the presence of strength are customarily used in determining solubility of essential oil. In preparing dilute alcohols it is convenient to weight the alcohol (95% by volume) and the distilled water to give the proper volume percentage. Preparation in this manner is independent of temperature. The strength of alcohol may be checked by sykes hydrometer, alcoholmeter or by determining the specific gravity.

Procedure

Take exactly 1.0 ml. of the oil in the 10ml. of glass stoppered measuring cylinder (calibrated to 0.1 ml) and place it in a device in which the specified temperature of the oil can be maintained. Add the dilute alcohol (Strength stated for the oil under test) with frequent and vigorous shaking. Record the volume of the ethanol required producing a clear solution.

Optical rotation

Optical rotation refers to angle through which the plane of polarized light is rotated by a column 100 mm. thick of the material under test at a specified temperature. The wavelength of the radiation used should be 589.30.3 mm. Most essential oils when placed in a beam of polarized light possess the property of rotating the plane of polarized light to the right (Dextrorotatory) or to the left (laevorotatory). This change in direction is known as optical rotation. The angle of rotation is dependent upon the nature of the liquid, the light used and the temperature. Both the degree of rotation and its direction are important as criteria of purity. In recording rotations it is customary to indicate the direction by the use of a plus sign (+) to indicate dextrorotation (rotation to the right i.e. clockwise) and minus sign (-) to indicate leavo rotation (rotation to the left i.e. anticlockwise). The extent of the optical activity of oil is determined by a polarimeter and is measured in degrees of rotation.

Apparatus

Polarimeter: Precision within 0.03 if it is properly adjusted it should give a reading of 0^0 and also of 180^0 with distilled water.

Light Source: Any device giving monochromatic light of wavelength 589.3 nm are used. Sodium vapor lamp is recommended.

Polarimeter tubes: When the determination is to be carried out at a specified temperature, use the Polarimeter tubes provided with a jacket for circulating water, with a suitable thermometer pocket incorporated in the jacket. If the determination has to be carried out at room temperature any other type of Polarimeter tube may be used. The length of tubes generally employed shall be 1000.05 mm. For lightly coloured material tubes of 2000.05 mm. and for strongly coloured or highly optically active materials tubes of 50 or 250.05 mm. are employed.

Device of temperature maintenance: When the determination is to be carried out at specified temperature, water at a suitable temperature shall be passed through the jacket surrounding the Plarimeter tube in order to maintain the material at the specified temperature 0.2^0C. during the observation.

Calculation

The optical rotation shall be expressed in circular degrees to the nearest 0.01^0C. Dextrorotary optical rotations shall be given (+) and the laevorotatory the negative (-) sign. If fractions of the degree are read on a scale marked in minutes, calculate the decimal equivalents.

Specific rotation

The optical activity of the material in a solution determined at a particular temperature and spectral line of light source is called specific rotation. Dissolve the material in rectified spirit reserving a separate portion of the solvent for a blank   determination. Make at least five readings of the rotation of the solution at 271^0C. Replace the solution with the reserved portion of the solvent, make the same number of readings and determine the average, which shall be zero point value. Subtract the zero point value from the average observed rotation, if the two figures are of the same sign or add if opposition in sign, to obtain the corrected observed rotation.

Calculation

$$\text{Specific rotation (d)} = \boxed{\frac{100\ a}{1pd}} = \boxed{\frac{100\ a}{1pd}}$$

Where:

A= The corrected observed rotation in degrees of the solution at temperature t c, using D line of sodium or yellow green line of mercury as the case may be.

1= The length in mm of Polarimeter tube.

d= The relative density of the material at the temperature of observation (t).

p= The concentration of the material expressed as grams of active substance in 100 gms. of solution.

c= The concentration of material expressed as the number of grams of active substance in 100 ml. of solution.

Refractive index

Refractive index is defined as a ratio of the sin of the angle of incident to the sin of the angle or refraction when a ray of light of defined wavelength passes from air to the material kept at constant temperature. For measuring refractive index of oil, usually abbe's Refractometer is used. The ABBE type of refractometer with a range of 1.3 to 1.7 is recommended for the routine analysis of essential oil. It has a prism and an eyepiece with magnifying glass. It has a cavity around the prism to circulate hot or cold water required to maintain it at a certain temperature and a hole in it to fit a thermometer for reading the temperature at which the Refractive index reading is taken. Usually refractive index reading is taken at 27^oC except for those, which are not liquid at this temperature, in which case a high temperature (30^oC say) depending on the melting point of the material shall be used.

Open the prism clean with soft cotton and place a drop of the oil to be tested on one part of the prism and close. Now, look through the eyepiece and turn the compensator knob until the colored indistinct boundary seen between the light and dark fields becomes a sharp line. Now adjust the knurled knob until the sharp line exactly intersects the midpoint of the cross wires in the image. Read the refractive index from the magnifier index pointer.

The refractive index n t/D at the specified temperature is given by the following formula:

$$Nt/D = nt'_D + 0.0004\ (t'-t)$$

Acid value

Most of the essential oils contain only small amounts of free acids. The acid value or acid number of oil is defined as ***"number of milligrams of potassium hydroxide required to neutralize the free acids contained in 1 gm. of the perfumery material".*** The acid value of oil often increases as the oil ages, expecially if the oil is improperly stored. Processes such as oxidation of aldehydes and hydrolysis of esters increase the acid value. Oils which have been thoroughly dried and which are protected from air and light show little change in the amount of free acids.

R COOH+KOH----------------------------------->RCOOK +H_2O
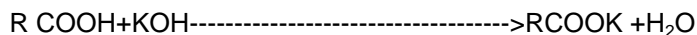
Calculation

$$\text{Acid value} = \boxed{\dfrac{56.1 \times V \times N}{M}}$$

Where

V = Volume in ml. of potassium hydroxide solution.
N = Normality of the potassium hydroxide solution.
M = Mass in gm. of the material taken for the test.

Ester value, content of esters and combined alcohols

The determination of the ester content is of great importance in the evaluation of many essential oils. Most esters, which occur as normal constituents of essential oils, are esters of monobasic acids. Ester value may be defined as ***"the number of milligrams of potassium hydroxide required to neutralize the acids liberated by the hydrolysis of esters present in 1 gm. of the perfumery materials".***

Calculation

Ester value=Saponification value – acid value.

Saponification value = $\dfrac{56.1 \times N \times (V_1 - V_2)}{M}$

Where
N = Normally of hydrochloric acid used for titration.
V_1 = Volume in ml., of hydrochloric acid used for the blank.
V_2 = Volume in ml. of hydrochloric acid used in determination.
M = Mass in gm. of the material take.

Ester content

The percentage of esters present in the material may be calculated as given below.

Ester (percent by mass) = $\dfrac{E \times M}{561}$

E   = the observed ester value.
M = molecular mass of the ester.
It is assumed that the alcohols are monohydric and the acids are monobasic.

Combined alcohol

The percentage of alcohols combined as esters in the material may be calculated as follows:
Combined alcohols (percentage by mass) = $\dfrac{E \times M}{561}$

Where
E   = the observed ester value.
M = molecular mass of the ester.
1. If the material contains phenols or compound with Phenolic groups use phenol red as an indicator instead of phenolphthalein
2. If the material used for the determination of ester value of the contents is reserved from the acid value determination then saponification value is the ester value.

Ester value after acetylation and free alcohols

The ester value after acetylation may be deinfed as ***"the number of milligrams of potassium hydroxide required to neutralize of acid liberated by the hydrolysis of 1 gm. of acetylated perfumery material".***

The alcoholic constituents of an essential oil are determined by acetylation i.e. the oil is acetylated with acetic anhydride in the presence of sodium acetate followed by alkaline hydrolysis and ester content of the resulting oil is determined from this value. The percentage of alcohol in the original oil may be calculated.

Calculation:
1) Ester Value after acetylation $= \dfrac{56.1 \times NX (V_1 - V_2)}{M}$

Where

N = Normality of hydrochloric acid used for titration

V_1 = Volume in ml. of hydrochloric acid required for the blank determination.

V_2= Volume in ml. of hydrochloric acid required to neutralize the excess alkali after   hydrolysis of the perfumery material.

M = Mass in gm. of acetylated material.

It is assumed that the alcohols are monohydric and the acids monobasic.

Content of the free alcohols (Uncombined) percent by mass $= \dfrac{M \times (Ea-Eb)}{561-0.42\ Ea}$

Where

Ea = Ester Value of the material after acetylation.

Eb = Ester value of the material before acetylation.

M = Molecular mass of the specified alcohol.

Carbonyl value by hydroxyl ammonium chloride method

The Carbonyl value of a perfumery material is the mass of potassium hydroxide inmg. that is equivalent to the mass of hydroxylamine required to oximate the carbonyl compounds present in 1 gm. of the oil.

The carbonyl compounds to be determined are converted into oximes by reaction with hydroxyl ammonium chloride. The hydrochloric acid liberated during the reaction is determined by an ethanolic potassium hydroxide solution.

Calculation

The carbonyl value and content of carbonyl compounds are calculated as follows:

Carbonyl Value $= \dfrac{56.1 \times V \times N}{M}$

Where,

   V   =   Volume in ml. of ethanolic potassium hydroxide solution used in determination.

   N   =   the normality of the ethanolic potassium hydroxide solution used.

Content of carbonyl compounds (as aldehyde or ketones)$= \dfrac{M \times VxN}{10m}$

   Where

   M = Molecular mass of the carbonyl compounds in which the results are to be expressed.

   V = Volume in ml. of ethanolic potassium hydroxide.

   N = the normality of the ethanolic potassium hydroxide solution used.

   M =   Mass in g of the sample.

GAS LIQUID CHROMATOGRAPHY

The basis for gas chromatographic separation is the distribution of sample between two phases. One of these phases is a stationary bed of large surface area, and the other is a gas, which percolates through the stationary bed.

Gas chromatography is a technique for separating volatile substance by percolating a gas stream over a stationary phase. If the stationary phase is a solid we speak **Gas solid chromatography. (G.S.C.).** This depends upon the adsorptive properties of the column packing to separate sample, primarily gases. Common packing used is silica gel, molecular sieve, and charcoal. In the **(G.L.C.)** the liquid is spread as a thin film over an inert solid and the basis for components to the separated are carried through the column by an **inert gas**

(carrier gas). The sample mixture is partitioned between the carrier gas and a non-volatile solvent (Stationary phase) supported on an inert size graded solid (solid support). The solvent selectively separates the sample components, according to their distribution coefficient; until they form separate bands leaving the column in the gas stream and recorded as a function of time by a detector.

The basic parts of the gas chromatograph:
1. Cylinder of Gases.
2. Flow controller and pressure regulator.
3. Injection part (sample inlet).
4. Column.
5. Detector (With necessary electronics).
6. Recorder.
7. Thermostat for injector, column and detector.

STORAGE OF ESSENTIAL OILS

It is one of the most important aspect, without which this manual will be incomplete though it is not directly related to the topic but it's importance is very much. Very less is known about the processes which cause the spoilage of essential oils. Usually they are following reactions:

(a)   Oxidation.
(b)   Resinification
(c)   Polymerization
(d)   Hydrolysis of esters.
(e)   Interaction of functional groups.

The above process are activated by following attributes

(i)   Heat.
(ii)   Air (oxygen)
(iii)   Moisture.
(iv)   Light.

Essential oils are in general colourless, particularly when they are fresh, but on storage they may developed colour. To prevent this following aspects are to be taken into consideration.

(a)   Protection from sun light.
(b)   Storage in a cool place.
(c)   Storage in dry environment.
(d)   Stored in a amber coloured bottles.
(e)   Bottle should be filled up to brim.

The high terpene content of citrus oils, pine needle oil, tagetes, turpentine etc. are very much prone to oxidation and resinification. Light is less harmful than moisture. Essential oil of lavender and Bergamot which contain high percentage of ester (linallyl acetate) turns acid after improper storage, during partial hydrolysis of ester. The aldehyde content gradually diminishes in case of oil of lemongrass and this process is much faster if aldehyde is stored after isolation from oil. This is probably due to presence of some antioxidant in oil. Oils containing alcohol like sandalwood, Geranium are quite stable and can withstand prolonged storage.

Essential oil should be freed from metallic impurities and moisture, only then it should be stored in well-filled tightly closed container, at low temperature and protected from light. For small packing amber coloured glass bottles are suitable but for large quantities they should be stored in metal drums, like tin lined if possible. A layer of carbon dioxide or nitrogen gas is blown inside container before it is sealed in order to replace air above oil and hence to protect it from oxidation.

In order to remove moisture which is one of the worst factor in the spoilage of essential oil the smaller lots can be made free from moisture by addition of anhydrous sodium sulphate, by thoroughly shaking, keeping aside and then filtering. Calcium chloride should not be used for removal of moisture as it forms complex salt

with certain alcohols. In case of viscous oil like Vetiver the problem of moisture could be tackled by addition of common salt and then allowing mixture to stand until supernatant oil has become clear. The lower layer could be filtered.

Centrifuging in high-speed centrifuges (rpm greater than 15,000) is an excellent mode of clarifying the oils. If, it is done along with freezing it can also remove waxes. In case of metallic impurities for oils like Clove, Bay the tartaric acid is employed and then filtration is done.

CHEMISTRY OF ESSENTIAL OILS

Essential oils are complex mixtures of sometimes hundreds of chemical compounds. Most of these compounds can be grouped into a few major classes but there are also many components of essential oils that bear little resemblance to these classes. In the overview of important and characteristic components given below, compounds are classified into four major groups: aliphatic compounds, terpenes and terpene derivatives, benzene derivatives and miscellaneous compounds [19].

Aliphatic Compounds

Aliphatic compounds are acyclic organic compounds. The chain of C-atoms in these compounds may be straight or branched and some of the bonds between C-atoms may be unsaturated. Aliphatic hydrocarbons occur abundantly in foodstuffs such as fruit but contribute to their odour to a limited extent only. The highly unsaturated hydrocarbons 1,3-trans-5-cis-undecatriene and 1,3-trans-5-trans-undecatriene however contribute significantly to the odour of galbanum oil. The odour of most aliphatic alcohols is weak and their role as components in fragrance compositions is limited. Of the aliphatic ketones, only 3-hydroxy-2-butanone (acetoin) and diacetyl (2,3-butanedione) are widely occurring natural isolates that play a role in flavouring. Both have a buttery aroma. Aliphatic aldehydes are important compounds in perfumery and flavouring. The unsaturated trans-2-hexenal or leaf aldehyde occurs in many leaf oils and has a sharp herbal green, somewhat pungent odour. Aliphatic esters are important flavour and fragrance compounds occurring widely in nature.

Terpenes and Terpene Derivatives

Terpenes constitute a widely represented group of substances. They are built from 2(monoterpenes), 3(sesquiterpenes) or more isoprene (C_5H_8) units. The terpene hydrocarbons contribute to the odour and taste of essential oils to a limited extent only but their oxygenated derivatives are among the most important aroma chemicals.

Monoterpenes

Monoterpenes conform to the molecular formula $C_{10}H_{16}$ and can be acyclic, monocyclic or bicyclic. There are very few tricyclic monoterpenes: cyclofenchene and tricyclene.

Acyclic monoterpenes

Acyclic monoterpenes are relatively unstable and some have a slightly aggressive odour because of their strongly unsaturated structure. Examples of acyclic monoterpenes include myrcene and ocimene.

Cyclic monoterpenes

Cyclic monoterpenes occur in essential oils sometimes in considerable amounts. They generally contribute relatively little to the odour of a fragrance or flavour product but often serve as starting materials for the biological or chemical synthesis of flavour and fragrance compounds. Examples of monocyclic terpenes are: α-terpinene, γ-terpinene or para-menthadiene, limonene, α-phellandrene and terpinolene. There are five types of bicyclic terpenes characterized by thuyene, carene, pinene, camphene and fenchene. The α-pinene and β-pinene are technologically the most important bicyclic terpenes.

Sesquiterpenes

Sesquiterpenes are compounds generated from 3 isoprene units and conforming to the formula: $C_{15}H_{24}$. As there are so many it is impossible to generalize about their molecular structure. Farnesene is an example of acyclic sesquiterpene. Many sesquiterpenes are bicyclic, having two C_6 and a C_5 ring; an extreme example is the monocyclic humulene with a C_{11}-ring.

Oxygenated Monoterpenes and Sesquiterpenes

Oxygenated derivatives of monoterpenes and sesquiterpenes are more important than terpene hydrocarbons as aroma chemicals. The characteristic odour of many essential oils is representative of the combined odours of the oxygenated compounds. Important groups of oxygenated compounds are alcohols, aldehydes, ethers, ketones, acids and esters. Acyclic monoterpene alcohols and acyclic sesquiterpene alcohols occur in many essential oils and contribute strongly to their characteristic odour. Some of them such as citronellol, geraniol, linalool and nerol are also synthesized from turpentine on an industrial scale. The most important aldehydes derived from acyclic monoterpenes and sesquiterpenes are citral and citronellal and hold key positions in many flavour and fragrance materials. Both are important starting materials for the synthesis of other aroma compounds.

Cyclic terpene derivatives are numerous and diverse. Cyclic terpene aldehydes occur in essential oils in low concentrations only, cyclic ketones are more important. Menthone and carvone, both of which have the para-menthone structure, are commercially important flavour and fragrance compounds. Ionones and homogenous compounds are an important group of terpenoid aroma chemicals. They are derived from carotenoids and are present in essential oils in small amounts only. Esters of terpene alcohols and lower fatty acids, in particular acetates, are highly important as flavour as well as fragrance materials. The esters of acyclic terpene alcohols citronellol, geraniol and linalool occur in large number of essential oils. Esters of cyclic terpene alcohols, such as α-terpenyl acetate, menthyl acetate, bornyl acetate and a few acetates of sesquiterpene alcohols, such as guaiyl acetate, cedryl acetate and vetyveryl acetate, are also important components of essential oils and are applied extensively in flavour and fragrance materials. Alcohols are often acetylated in essential oils, to modify their olfactive characteristics.

Benzene Derivatives

It is a very large and varied group that includes many natural and synthetic flavour and fragrance compounds. The most important hydrocarbon derived from benzene is paracymene, it occurs in many essential oils. Of the benzenoid alcohols and aldehydes, important components of essential oils are phenylethyl alcohol, cinnamic alcohol, cinnamic aldehyde and phenylacetaldehyde. Esters of aromatic alcohols and aliphatic acids are of interest in flavours and fragrances because of their characteristic odour properties. Benzyl acetate is the main component of jasmine oil and gardenia oil, phenylethylacetate is an aroma compound found in several essential oils and in many fruits, benzyl benzoate is a major component of Peru Balsam and is commonly used as fixative and modifier of heavy blossom fragrances in perfumery.

APPLICATIONS OF ESSENTIAL OILS

Essential oils or volatile or ethereal layer of oils, find as wide and varied application in many industries for the scenting and flavoring of all kinds of 'consumers' finished products, some of them luxuries, most of them necessities in our advanced civilization. Many of these products contribute directly to our health, happiness and general well being. Most obvious role of essential oils is as fragrance materials but they are equally important as flavoring materials and in medicine (Table 1).Perfumes are often used to favourably influence mood; aromatherapy goes further by exploiting this to create a soothing, tranquillizing or healing effect on a patient. Spices, which have volatile oil as their flavour principles, have long been used as flavoring materials but few of us realize that they are actually indispensable in bringing about proper digestion of food. The digestive juices containing digestive enzymes such as pepsin, trypsin, lipase, amylase etc. are secreted into the stomach and intestines only when stimulated by the smell and taste of pleasantly flavored food.

Pharmacological, clinical tests and experiences of the traditional medicine prove the importance of essential oils in driving out diseases. Essential oils have the following effects on external application: hyperaemic, antiinflammatory, antiseptic, granulation stimulating, deodorizing, insecticide and repellent actions.

On oral application the following effects are observed: expectorating, appetite stimulating, choleretic, cholekinetic, carminative, spasmolytic, antiinflammatory, antiseptic, diuretic, sedative and circulation stimulating. The main side effects of essential oils are allergic reactions; some oils have phototoxic effects, only a few essential oils show necrotic, narcotic, nephrotoxic, hepatotoxic and cancerogenic actions. In many cases the side effects are purely toxic effects caused by misuse of essential oils. Essential oils are also sources of many constituents that are used for more specific purposes. Linalool, one of the most widely occurring compound in essential oils, is an important source material for the production of vitamin E; citral another important component of several essential oils, has long been used to produce vitamin A.

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