6. Oils, Fats and Detergents

6.1 Introduction to oils, fats and detergents

What are fats, oils and detergents?

Fats, oils and detergents are materials of great industrial as well as household applications. Even though there exists little similarity as far as the chemistry of oils and fats (on the one hand) and the detergents (on the other hand) are concerned.

Generally speaking, organic substances that are either solids or get solidified at lower temperatures (for example, at ambient temperatures) are termed as fats, provided they are meant for edible purposes. That is how one can differentiate fats from waxes inspite of the fact that fats are also waxy and waxes do have the basic physical characteristics such as solidification at lower temperatures, a behavior similar to fats.

Unit objective

At the end of this unit students should be able to:

- Describe the difference and similarity b/n fats, oils and detergents
- Discuss the physical and chemical property of fats and oils
- Explain the factors affecting fats and oils
- See the difference in fats and oils reaction with hydrogen
- Analyze fats and oils
- Define detergents
- Classify detergents and explain their action
- See the difference b/n soaps and detergents

What are oils? Can coconut oil, which solidifies at lower temperature, be considered as fats?
The biggest questions are, are fats and oils the same?

Dealing with food products and taking it further from just the criteria of solidification at lower temperature, one will have to really look into it, in a little more detail, in order to explain the difference between fats and oils.

In India, the cream separated from milk is known as “ghee”. The same product is popularly called “Butter Oil” in the western countries. How do we explain this difference in perception about a given product? Let us take an example of hydrogenated fat.

In India, we call the hydrogenated fat also as “ghee” whereas in Europe, it is called mostly as hydrogenated fat and rarely as hydrogenated oil.

Let us take the example of kerosene, which is commonly known as oil. The organic can easily be put into two major categories:

a) Those soluble in water are non-oily and b) Those insoluble in water are oily. Because kerosene is oil, people started calling it as oil.

Now, the question arises, whether kerosene can be put in the same category as soybean, ground nut, and mustard oils. Certainly not!

The oily substances would obviously include fats, (which includes the organic substances solidifying at lower temperatures and which are edible) as well as oils (which includes butter oil, vegetable oils and also kerosene oil) and hence, it should be the criteria to define or name substances.

It is always better to define substances based on their chemical structure. It is only the triglycerides which are defined as oils and fats.

Detergents are basically the substances, which have the tendency to exist equally (or partially) in both– the oil medium as well as in the water medium, and such substances are exploited for their use to stabilize multiphase systems. Both the hydrophilic and hydrophobic moieties coexist in the molecule of a detergent. As a result, such substances can reorient themselves in the multiphase systems depending upon the polarity of different phases.

6.2. Properties of oils and fats

Physical Properties of Fats and Oils

♦ **Melting and freezing points**

The melting point and freezing point of fatty acids increases with increasing degree of saturation as well as with increasing the carbon chain length. As a result, the triglycerides based on fatty acids also follow a similar trend of melting point. From the melting behavior of the fats and oils, one can make an idea of their type as well as their source.

The melting point also depends upon the polymorphic form of the glycerides. The solidification point is generally lower than the melting point and the solidification behavior can also be used for characterization of fats and oils. Since the naturally occurring fats and oils are a mixture of glycerides, they melt over a wide range of temperatures.

♦ **Thermal property**

The specific heat of oils and fats increases with the increase in chain length and degree of saturation in the carbon chain of the fatty acid. It also increases with temperature. Oils and fats are relatively poor thermal conductors. The smoke, flash and fire points are measures for their thermal stability when heated in air.

♦ **Density**

The density of fatty acids and hence, of the triglycerides decreases with increasing molecular mass and degree of saturation. Oxidation of the triglycerides generally leads to higher densities. High free fatty acid content lowers the density of a crude oil and hence, density can be criteria for quality of fats and oils.

♦ ***Viscosity***

Oils tend to have a relatively higher viscosity because of intermolecular hydrophobic attraction between their fatty acid chains. Generally, viscosity tends to increase slightly with increasing carbon chain length.

♦ **Solubility and miscibility**

Nearly all fats and oils are easily soluble in common organic solvents such as hydrocarbons, chlorinated hydrocarbons, ethers, and acetone. However, the solubility of fatty acid is greater than that of their corresponding triglycerides. The water solubility of fats is low and decreases with increase in carbon chain length and with the increase in the degree of saturation.

Factors affecting Characteristics of Fats and Oils

The characteristics of fats and oils depend upon the degree of saturation, the length of the carbon chain, isomeric form of the fatty acids, molecular configuration, and the type and extent of processing.

Degree of unsaturation of fatty acids

Degree of unsaturation of fatty acids forming the triglycerides plays an important role in deciding the characteristics of fats and oils. That is why, the fats and oils are also classified based on the number of double bonds present in the carbon chain of the fatty acid; mono-, di- and tri-unsaturated fats for the presence of one, two and three double bonds in the chain respectively.

Fats with higher number of double bonds (unsaturation) are also called as poly unsaturated fats or PUFA fats. From the health point of view, the consumption of PUFA fats are recommended over the others, for example, MUFA fats (mono unsaturated fats). For the determination of degree of unsaturation, fats and oils are checked for their capacity to absorb the quantity of iodine per unit weight of the fats. The average iodine value (amount of iodine absorbed per unit weight) of natural fats and oils is 125-140.

Length of carbon chain in fatty acids.

The length of the carbon chain of the fatty acid has the bearing on most properties of fats and oils. For detailed characterization of fats and oils, it is important to study the distribution of carbon chain length of their fatty acids.

Isomeric forms of fatty acids.

Isomeric form of the fatty acid also affects the behavior of triglycerides. For example, oleic acid is liquid even at temperature lower than room temperature where as its isomeric form elaidic acid is solid at temperatures much higher than room temperature.

Polymorphism

Solidified fats exhibit polymorphism, i.e., they exist in several different crystalline forms, depending on the manner in which molecules orient themselves in the solid state. The crystal form of fats can be transformed from lower to higher melting modifications. The rate of transformation and the extent to which it proceeds are governed by the molecular configuration and composition of the fat, crystallization conditions, and the temperature and duration of storage. The crystal form of the fat has a marked effect on various properties of fats.

6.3 Classification of Fats and Oils

On the basis of applications

There are various ways in which the fats and oils have been classified. The first criteria of classification have been the edible nature; edible fat and non-edible fat. . Fats in the diet are also referred to as visible or invisible; visible fats are those added to the diet in foods such as dressings, spreads, whereas invisible fats are those which occur naturally in foods such as meat and dairy products. While the classification of fats and oils is done based on their chemistry and chemical composition, they are also known by several names, depending on their applications as drying oils, non-drying oils, semi-drying oils, etc.

Drying Oils: The fats having a large proportion of unsaturated acids have the tendency to get solidified on exposure to air. This property is also known as drying behavior. The oils, e.g., linseed, hemseed, and poppy seed oil, are the prominent drying oils and they are used in making paints and varnishes.

Non-drying Oils*:* Vegetable oils such as olive, rapeseed, and castor oil and animal oils such as lard oil and neat’s foot oil do not possess this property of drying oils and are classified as nondrying.

***Semi-drying oils**:* Those which can neither be termed as completely drying nor as completely non-drying are called as semi-drying oils. This type of classification, however, fails to take into account a number of important distinctions within the three broad classes.

There is another well recognized criteria for classification of fats and oils that deals with the degree of unsaturation of the fatty acid chain and fats are categorized as saturated, monounsaturated and polyunsaturated.

***On the basis of saturation**.*

Saturated: A fat or oil is saturated when all available carbon bonds are occupied by hydrogen atom. They are highly stable, because all the carbon-atom linkages are filled or saturated with hydrogen and hence they do not normally go rancid, even when heated for cooking purposes.

They are straight in form and hence, pack together easily, so that they form solid or semisolid fat at room temperature. Butyric acid is an example of saturated fat found in the fat derived from milk.

***Monounsaturate**d:* Monounsaturated fatty acids have one double bond which means that such acids lack two hydrogen atoms in comparison to the saturated acid on each of the two carbon atoms of the fatty chain. The human body can make monounsaturated fatty acids (MUFA) from saturated fatty acids and use them in a number of ways. Such fats have a kink at the position of the double bond so that they do not pack together as easily as saturated fats and, therefore, tend to be liquid at room temperature.

Polyunsaturated: Such fats have two or more pairs of double bonds, as Trilinolein, therefore, lack four or more hydrogen atoms. Such fats have a kink at more positions than in MUFA so that they do not pack together. They are liquid even when refrigerated. The unpaired electrons at the double bond make these oils highly reactive. They go rancid easily and should not be used for cooking. Polyunsaturated fatty acids are usually found in cis form.

All fats and oils, whether of vegetable or animal origin, are combinations of triglycerides based on saturated fatty acid, monounsaturated and polyunsaturated fatty acids. Vegetable oils from the plants grown in hot climates are more of saturated type because the increased saturation helps maintain stiffness in plant leaves. Besides the above mentioned ways of classifying fats and oils, there is yet another widely accepted basis of classification which primarily deals with the origin or source, carbon chain length and some unique feature of fats and oils.

On the basis of carbon chain length

Short Chain fatty acids, generally, mean four to six carbon atoms and they are always saturated. These fatty acids have anti-microbial properties. They do not need to be acted upon by the bile salts but are directly absorbed for quick energy. For this reason they are less likely to cause weight gain and also contribute to the health of the immune system. Butyric acid is an example of short chain fatty acid, which is found present for example, in the fats from milk. The fats and oils based on short chain fatty acids are known for their health benefits.

Medium Chain fatty acids have eight to twelve carbon atoms and are found mostly in butter fat and oils produced from plants grown in tropical regions. They too have antimicrobial properties and they are absorbed directly for quick energy; and contribute to the health of the immune system. Lauric acid, the main component of the triglyceride in coconut oil is an example of medium chain fatty acid with 12 carbon atoms. For several advantageous attributes of coconut oil, it is a preferred cooking medium in many parts of the world.

Long Chain fatty acids have 14 to 18 carbon atoms and can be different types such as saturated, monounsaturated or polyunsaturated. For e.g. Palmitic acid with 16 carbon atoms, stearic acid and oleic acid with 18 carbon atoms are the examples of long chain fats with different degrees of saturation.

From the standpoint of their Industrial production as well as their utilization, fats and oils are more rationally divided into the following groups.

Milk fat: The fats of this group are derived from the milk of domesticated land animals for example, cow, buffalo, goat, etc. Principal fatty acids in such fats are palmitic, stearic and oleic acids with minor presence of butyric acid.

Vegetable butter: They are obtained from the seeds of various tropical trees. They all contain mostly the saturated C12 to C18 acids. The representative fat of this group is cocoa butter.

Animal fat: This group consists of the body fats of mainly the domestic land animals (lard, tallow, etc.). These fats have high content of C 16 and C18 fatty acids and a low degree of unsaturation. They contain considerable proportions of fully saturated triglycerides, which give them an extended plastic range. They are important edible fats but because they are derived from animals and parts of carcasses, in some cases, when they are considered as unfit for human consumption, they are used in the manufacture of industrial products such as soap, for which they are considered as an important ingredient.

Lauric acid group: The fats of this group are derived from the seeds of species of plants such as the coconut and babassu. They contain smaller amounts of saturated acids with carbon chain length of 8 to 14. The content of unsaturated acids is very less; they are the least unsaturated of all the industrially important fats.

Oleic- Linoleic acid group **–** The oils of this group are mainly of vegetable origin. They consist predominantly of unsaturated fatty acids which consist of oleic and linoleic acids. Most members of this group are liquids except at quite low temperatures. They are not sufficiently unsaturated to have more than weakly drying properties, so they are not used to any great extent in paints and other protective coatings. They are excellent edible oils. These oils may also be considered as medium priced fats. More important members of the oleic-linoleic acid group include cottonseed, peanut, sesame, corn, palm, olive, sunflower and safflower.

Erucic acid group: The members of this group, of which only mustard, ravison, and rapeseed oil are commercially important, are distinguished by a high content (40-50%) of erucic acid. In comparison with other vegetable oils, these oils are normally cheap and thus, become the prefered choice for common people as edible oils. There have been studies which show that the mustard oil is very good for health. The efforts to develop the mustard oil with minimum possible content of Erucic acid have always found support from all the stake holders.

Linolenic acid group: The oils of this group are distinguished by a significant amount of linolenic acid, in addition to oleic and linoleic acid. The most important members are derived from the seeds of annual plants. These oils have drying properties and hence, are used in paints and similar products. Because they tend to revert in flavor with slight oxidation, these oils are not considered as desirable for edible purposes for which only the oleic-linoleic acid oils are suitable. They are cheaper than oleic-linoleic acid oils. The most important members of this group are linseed, perilla and hempseed oil.

Conjugated acid group: The oils of this group are differentiated from others by the presence of fatty acids with conjugated double bond. The commercially important members are tung oil and oiticica oil which are derived from seeds of trees grown in a mild climate. Because of conjugated double bonds, which favor oxidation and polymerization, these oils dry more rapidly than ordinary drying oils. They are unsuitable for edible purposes but can be used for industrial applications such as paints, varnishes etc.

Marine oil group: These oils are distinguished by the diversity of their unsaturated fatty acids.
They contain large proportions of unsaturated acids mainly of 16 to 18 carbon atoms but with significant amount of the carbon chain longer than 18 carbons. The group comprises of fish oils and marine mammal oils, such as whale oil. These are the cheapest of all fats and oils. They are used in edible fat products but can also be used, in soap, and in protective coatings. Fish liver oils constitute a special class of oils, which are highly valuable as a source of vitamins A and D, and are used for edible as well as industrial purposes.

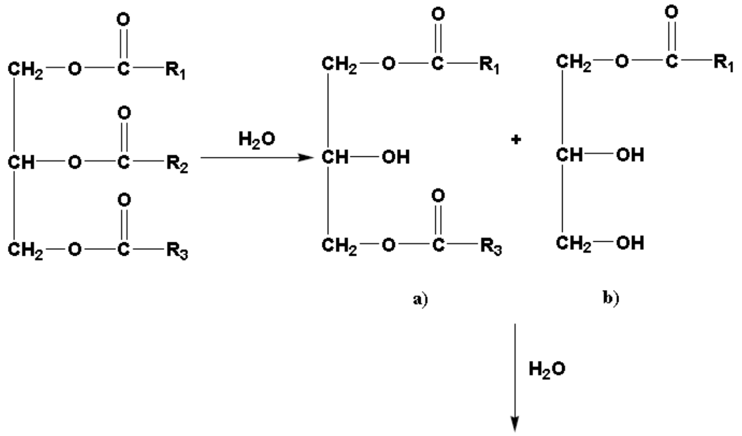
Hydroxy acid group: The sole representative of this group used commercially is castor oil which is unique as it consists largely of triglycerides of ricinoleic-2-hydroxyoctadecenoic acid. It is not an edible oil but it is used in several industrial applications such as lubricants, surfactants, oil for sulphonation, a fluid for hydraulic systems etc. From the above discussion, it may be noted that the same fat or oil may be classified under the different categories depending upon the basis of classification. Of course, there are only two basic categories of fats and oils; edible and non-edible.

Trans fat

Tran’s fat, as its name suggests consists of trans fatty acid which is an unsaturated fatty acid containing trans double bond between carbon atoms. The trans double bond of fatty acids are less kinked compared to those with cis double bond. A majority of trans fats are formed during the manufacture of processed foods. In unprocessed foods, most 0unsaturated bonds in fatty acids are in the cis configuration. Though some trans fats are found to be present naturally such as conjugated linoleic acid or CLA, these conjugated systems with trans linkages are not counted as trans fats for the purpose of nutritional regulations and labeling.

Partial hydrogenation increases the shelf life and flavor stability of foods containing these fats. Partial hydrogenation also raises the melting point, producing a semi-solid material, which is much more desirable for use in baking than liquid oils. Partially hydrogenated vegetable oils are much less expensive than the fats originally favored by bakers, such as lard or butter. Saturated and trans fats can be found together in some foods such as vegetable, shortenings,some margarines (specially margarines that are harder), crackers, candies, cookies, snack foods, fried foods, baked foods and other processed foods made with partially hydrogenated vegetable oils. High amounts of saturated fats are found present in animal products, such as beef and pork, chicken skin, butter, whole milk and cheese. Foods high in cholesterol include egg yolks and dairy fats.

Trans fat is an artery clogging fat that is formed when vegetable oils are hardened for example into margarine or shortening. It is found in many foods including fried foods. Trans fat is known to increase levels of low density lipoprotein (LDL) or bad cholesterol, while lowering levels of high density lipoproteins (HDL) or good cholesterol in blood. It causes clogging of arteries and it is believed to be responsible for type-2 diabetes and other serious health problems. It has been found to increase the risk of heart diseases because the trans fat is not recognized by the body’s metabolism, causing it to deposit in the blood vessels.



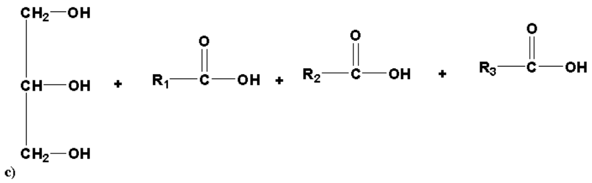


Fig 6.1: All the three ester groups have the equal possibility of hydrolysis. However, depending upon the pH, catalyst and enzymes, one or more of the ester groups get hydrolyzed. For example, a) in the case of only one ester getting hydrolyzed, it results in the formation of a diglyceride; b) in the case of two ester groups getting hydrolyzed, the end result is a monoglyceride and c) in the case of three ester groups getting hydrolyzed, formation of glycerol takes place.

Trans fats should not be completely eliminated from the diet because of the fact that it mayrequire extraordinary dietary changes that eliminate trans fats and cause inadequate intake of some nutrients which could create health risks. Trans fats are always compared with saturated fats in terms of their affect on blood cholesterol levels. Trans fats raise LDL blood cholesterol as much as saturated fat does. However, trans fats have lesser effect on total blood cholesterol than saturated fats.

Chemistry of trans fatty acids.

Trans fatty acids are made when manufacturers add hydrogen to vegetable oil, in the presence of small amounts of catalyst such as nickel, palladium, platinum or cobalt in a process called partial hydrogenation. If the hydrogenation process was allowed to go to completion, there would be no trans fatty acids. The resulting material would be too solid for practical use. However, partial hydrogenation reconfigures most of the double bonds that do not become chemically saturated, so that the hydrogen atoms end up on different sides of the chain. This type of configuration is called “trans”.

Increasing the pressure at which oil is hydrogenated reduces trans fat formation. Blended with pure soybean oil, the high pressure processed oil produce margarine containing 5-6 percent of trans fat which could qualify for a label of zero grams of trans fat.

6.4 Chemical Properties of Fats and Oils

Hydrolysis of fats and oils:

Like all esters, glycerides can also be easily hydrolyzed yielding mono and diglycerides (on partial hydrolysis) and glycerol and fatty acid (on complete hydrolysis). With sodium hydroxide, glycerol and sodium salt of fatty acid (soaps) are formed. The hydrolysis can also become possible through enzymes. In the digestive systems of animals and humans, fats are hydrolyzed by the enzyme (lipases).

Oxidation of fats and oils:

Autoxidation: Oxidation at room temperature is referred to as autoxidation and this is also referred to as rancidity of fats and oils. This is a slow process, which occurs only to a limited degree if fats and oils are left for storage. In this process, oxygen reacts with unsaturated fatty acid chains. Initially, peroxides are formed which in turn breakdown the chain of fatty acids into hydrocarbons, ketones, aldehydes, and small amounts of epoxides and alcohols. The result is objectionable flavor and odor. The fats and oils after autoxidation, therefore, become unsuitable for human consumption if the extent of oxidation is very high.

Oxidation at higher temperature: Differences in the stability of fats and oils often become more apparent when the fats are used for frying and baking. The more unsaturated the fat or oil is the greater will be its susceptibility to oxidative rancidity. It is precisely due to this reason that the re-use of the frying oils is not good for health, especially after the oil has been in the frying pan for a long time. Generally, the peroxide content is the criteria for checking the autoxidation or rancidity of fats and oils.

Polymerization of fats and oils:

Fats, particularly those with, high content of polyunsaturated fatty acids tend to form larger molecules (known as polymers) when heated under extreme conditions of temperature and for an extended time period. Under normal processing and cooking conditions, polymers are formed in insignificant quantities. Polymerization takes place through the double bonds between the carbon atoms or by oxygen bridges between molecules. When polymerization takes place there is a marked increase in viscosity of the oils. In any case, polymer, present in the fat or oil are absorbed poorly by the intestinal tract and removed as such from the body.

Hydrogenation of fats and oils:

The fats which are liquid at room temperature preponderate in nature over those which are solid. To meet the demand of solid fats, therefore, one has to make an effort. Taking advantage of the experience where the ethylenic organic compounds when exposed in the vapor state to hydrogen in the presence of nickel formed the corresponding saturated derivatives, the unsaturation in fats were also subjected to the hydrogenation. Liquid fats and fatty acids having unsaturated bonds could also be hydrogenated in a similar way using nickel, palladium, copper, or platinum and the liquid oil was converted into solid form.

Hydrogenation is the single largest chemical reaction in the fatty oil processing industry. Since each double bond may be either isomerized or hydrogenated at different rates depending on its position or environment in the molecule, the overall reaction becomes quite complex. The partial hydrogenation of soybean oil would result in at least 4000 different triglycerides.

Primarily, hydrogenation is a means of converting liquid oils to semisolid fats suitable for shortening or margarine manufacture. It also accomplishes various other desirable purposes, including enhancement of the stability and the improvement of the color of the fat. However, the hydrogenation of fats and oils is also associated with some disadvantages. If fats are subjected to the action of hydrogen in the presence of an appropriate catalyst at relatively higher temperature and at a very high pressure during the hydrogenation, fatty alcohols are also formed. Higher fatty alcohols are in demand nowadays because their sulphates and phosphates possess very valuable properties as detergents, emulsifiers, wetting out agents, etc.

Since the ethylenic linkages in a highly unsaturated fatty acid occur at different points in the chain of carbon atoms, there is a formation of iso- acids in the glycerides of partially hydrogenated oils. The most objectionable properties of these acids are connected with their behavior as soaps. For example, whereas the oleic acid is an almost ideal constituent of soap by virtue of the relative solubility and low surface tension of solutions of its sodium salts, the lower solubility and much higher surface tension of the sodium salt of the iso-oleic acid does not allow it to exhibit the similar behavior. The iso-acid based soaps are inferior in lathering and detergent power to soap made from natural fatty acids of same degree of unsaturation and hydrogenation causes the formation of iso-oleic acid. As regards color, hydrogenated fats are usually superior to much natural fat and objections were raised to a specific color associated with soaps or fats containing hydrogenated material.

6.5 Production of Fats and Oils in Plants and Animals

The primary seat of the production of fats is in the vegetable kingdom; here, the carbohydrate material produced in the plant from carbonic acid and water by the agency of enzymes and sunlight are converted into fatty compounds, mainly during the period of ripening of fruits and seeds. The fats are deposited, in general, either in the tissues, which surround the embryo or germ of the seed, or in the external fleshy covering, in which the seed-capsule is enclosed.

In plants and animals, the fats are normally a form of reserve or storage of organic matter, which, at a later stage in the life cycle may be required for purpose of nutrition. In animals, fats are produced by assimilation of either the fats consumed as food or of the fats produced in the body through vital synthesis (enzymatically driven) involving various types of organic matter, such as carbohydrates, proteins, etc.

The formation of fats in the animal body is believed to take place mainly in the liver and related organs. The primary organic materials are converted into fatty acids and their esters, whilst fat already present as such may be hydrolyzed and re-built into esters with or without alteration in the constitution of the fatty acids originally ingested. The synthesized fat passes via the blood stream into various parts of the body- notably the flesh tissues near the skin in which it is stored.

In vegetable oils and fats, unsaturated fatty acids are linked to the 2- position of the glycerol group, whereas in animal fats they appear in 1 – and 3- positions.

6.6 Analysis of Fats and Oils

As stated above, the fats and oils consist of a major component (triglyceride) and various types of minor components. For any application, the processing of the crude fats and oils is essential.

For using fats and oils as food, it is not only important to process them but also to check their quality by analyzing them thoroughly. Analysis and characterization of fats and oils is done by using simple methods as well as sophisticated techniques such as HPLC, GLC, TLC etc. as depicted in standard methods of analysis of fats and oils to be used as food.

Saponification value

It is also a measure of the mean molecular weight of the fatty acid present in the fat. The process of saponification is the hydrolysis of triglycerides into glycerol and the potassium salt of the fatty acid, using an alcoholic solution of potassium hydroxide. The amount of alkali required to combine with the fatty acids liberated by the hydrolysis of the fat on saponification gives the equivalent weight as well as molecular weight of the fatty acids. The saponification value is expressed in milligrams of the potassium hydroxide required to saponify one gram of fat. For all the fats and oils, the limits for the saponification value are fixed and based on this one can easily identify the fat. For given fat, this can be a useful tool to check quality of fats.

Iodine value

Iodine number is the number of grams of iodine absorbed by 100g of the sample. It is a measure of the degree of unsaturation in the fatty acid chain. The test measures the amount of iodine which can be absorbed by the fats. As the addition of iodine takes place at the double bond measurement of the quantity of iodine absorbed gives the idea about the number of the double bonds present.

Unsaponifiable matter

Since the fats are triglycerides, they would saponify in the presence of alkali. But the fats and oils contain certain fraction which cannot be saponified; called as unsaponifiable matter. During this process, all the triglycerides are broken down to form glycerol and potassium salts of the fatty acids. Both of these products are water-soluble. But there is a third component which is water insoluble. The water insoluble component may consist of hydrocarbons, sterols and fatty alcohols, which are all unsaponifiable. The amount of unsaponificable matter found in eatables, fats, is supposed to be absent; high unsaponifiable may indicate contamination or adulteration.

Refractive index

It is a physical attribute of triglycerides, measured by the angle through which a beam of light is bent when passing through a thin film of melted fat. The index of each type of fat falls within a narrow range and it can be used as a characteristic of the fat in checking purity or searching for components of a mixture. It is temperature dependent and is usually measured at 40^0C, a temperature at which most fats are liquid. A correction factor can be used if it is not possible to work at a selected temperature for which reference data are available.

Melting and solidification temperature

As fats are a mixture of a number of different triglycerides, the melting point becomes difficult to measure. It is therefore necessary to impose an empirical test procedure, which will allow reproducible results to be achieved, but which cannot be used to identify components of a mixture. The two common measurements generally adopted are “slip point” and “titre”. The slip point measures the temperature at which a carefully prepared sample will move or slip in a capillary tube when heated slowly in a water bath.

The titre is not really a characteristic of fat itself, but is the solidifying point of the fatty acids prepared from the fat. It has some significance in soap-making technology but is of little importance in the examination of eatable fats.

The sample is melted and filtered to remove impurities. The molten product is taken in a melting point tube, placed in a beaker, which is then placed in a refrigerator for 16 hrs. The sample is removed and heated in a water bath till the liquid becomes completely clear. The temperature at which the sample becomes completely clear is noted as the melting point or titre value of the fat.

Impurities

Determination of impurities present is not as simple as it may appear. In principal, it is the measurement of solid matter, which is not soluble in fat. This is complicated because some insoluble materials may get dispersed in the fat. Such materials precipitate out when a suitable solvent is added during the estimation of impurities.

Acid value

It is a measure of the amount of free fatty acid present in fat. Some of the deterioration that takes place during storage of either the raw material from which the fat is obtained or in the fat itself after isolation results in hydrolysis of triglycerides to yield free fatty acids. As these free fatty acids must be removed in the preparation of eatable fats, the commercial yield will be reduced by an amount proportional to (but greater than) the amount of free fatty acid present.

Peroxide value

It is usually used as an indicator of deterioration (rancidity) of fats. As oxidation takes place, the double bonds in the unsaturated fatty acids are attacked resulting in peroxides. These break down to produce secondary oxidation products, which indicate a condition known as rancidity. The peroxide value can therefore be used to estimate oxidation but as the compound formed is unstable and oxidation proceeds further, it is not a complete measure of oxidation and if taken in isolation may give rise to misleading conclusions. In any case, peroxide value is one parameter based on which one can reject or approve the fats and oils for human consumption.

Nutritional Aspects of Fats and Oils

Fats are the most important constituents of our diet contributing about 38 J/g of energy as compared to 17 J/g provided by carbohydrates and proteins. The nutritive value of fats is dependent upon the number of carbon and hydrogen atoms, and on the ability to be absorbed in the body. If the fats are liquid at body temperature they are much more readily digested and absorbed than the ones which are solid. The ease of emulsification of fat is the important factor for its absorption. The nutritional value of fat also depends upon the presence of certain fatty acids, which were at first called vitamin F, and later as essential fatty acids.

Triglycerides for Indication of Health

The normal range of triglycerides in the blood depends upon the age and gender of the patients. Women naturally have high levels of triglycerides than men. Pregnancy also increases triglyceride level in women. As people age and gain weight, triglyceride levels generally increase. For adults, a normal level is considered to be less than 200 mg/dl. Levels from 200-400 mg/dl are considered borderline high. Triglycerides level ranging from 400-1000 mg/dl are considered high and levels greater than 1000 mg/dl are considered very high.

Extremely low triglycerides levels (less than 10 mg/dl) indicate malnutrition, malabsorption, a diet too low in fats, or an overactive thyroid problem. A triglyceride count in the 250-750 range indicates a high risk of heart disease. Because of the close relationship between triglycerides and cholesterol, the higher risk is from elevated blood/serum cholesterol levels. AIDS patients usually have low cholesterol levels, so a sudden increase may be related to triglyceride problem.

High blood levels of triglycerides result in the following cases:-

1) Carbohydrate sensitive people whose bodies have trouble breaking down fats or carbohydrates. 2) Obesity 3) Diabetes 4) Heavy alcohol drinkers

Many people with high triglycerides levels have low levels of ***high density lipoproteins***, called HDL or good cholesterol as it acts like a removal system for cholesterol. Low level of HDL is another risk factor for heart disease.

Triglyceride levels can be affected by any or all of the following factors:

1) Alcohol intake 2) Medicine 3) Hormones 4) Diet 5) Menstrual cycle
6) Time of day 7) Recent exercise

While there are several reasons for high triglyceride levels in the blood of humans, it is not in the scope of this chapter to elaborate on all those and their effects on the health of humans. However, the subject of interest is whether the high level of triglycerides in food products has any direct relationship with the high triglyceride levels in blood. The diet certainly plays an important role in keeping the triglyceride levels in blood under control. What should be eaten and what should not be eaten again depends on the metabolic system, exercise and the general health condition of the consumer. However, the following basic facts must be kept as the ground rule for controlling the glyceride levels in blood:

1. Use of fats and oils of different types, in varying proportions and in a controlled way.
2. Use of more of unsaturated fats than the saturated fats.
3. Avoid the trans fats as much as possible.

Cholesterol

Fat travels in the blood in two forms. One is **Cholesterol**, which is a structural fat. It glues cells together, insulates nerves and provides raw material for making hormones. Fat also travels in small energy packets, called triglycerides, which are further, coated with cholesterol. Cholesterol is a waxy substance that occurs naturally in the tissues of all animals. The human body needs cholesterol to function properly, such as producing vitamin D, bile acids (to digest fat) and many hormones. Given the capability of all tissues to synthesize sufficient amounts of cholesterol for their needs, there is no evidence for a biological requirement for dietary cholesterol.

Estimation of Fat Content

One useful measure of fat is the percentage of calories as fats in a diet. To compute this percentage, one needs to know both- the total calories and the grams of fat:

$$\%\ \text{CFF} \quad \frac{\text{grams of fats x 9}}{\text{total calories}} 0 \quad \text{x} \quad 100$$

%CFF= Calories from fat

Fat content of oils

All oils are 100% fats. These include olive oil, sesame oil, chilli oil, fish oil, avocado oil, walnut oil, etc. Oils and fats have been studied thoroughly and they are found to have 9 kilocalories per gram.

Dietary need for fat

It is absolutely true that we need fat in our diet to function properly. It would be unhealthy to eliminate all fat. All foods have fats but with varying content and of different types. A diet consisting only of beans, fruits, vegetable, and grains will naturally obtain about 6-10%CFF.

Foods labeled “fat free” can contain anywhere up to 0.5g of fats per serving and this shows that all foods contain some fat: even the skimmed milk!

How much fat do we need?

A diet with at least 10g of fats per day will result in normal vitamin absorption. However, it depends on the status of the health of the consumer.

Disadvantages of unsaturated fat

Unsaturated fats can exhibit different 3-D structures, notably a structural difference called cis-trans isomerism. Natural fatty acids have a cis form but on hydrogenation their form changes from cis to trans, which are known for their disadvantages as described earlier.

Importance of Fats and Oils

Fats and oils are recognized as essential nutrients in both human and animal diets due to the following reasons:

1. They provide the most concentrated source of energy than any foodstuff.
2. They supply essential fatty acids (which are precursors for important hormones, the prostoglandins),
3. They contribute greatly to the feeling of satiety after eating,
4. They are carriers for fat-soluble vitamins, and serve to make food more palatable.
5. Fats play a vital role in maintaining healthy skin and hair,
6. Fats insulate body organs against shock,
7. Fats help in maintaining body temperature and healthy cell function.
8. Fats also serve as the stock of energy stored in the body.

Fats are broken down in the body to release glycerol and free fatty acids. The glycerol can be converted to glucose by the liver and is thus used as a source of energy. The fatty acids are a good source of energy for many tissues, especially the heart, kidney and skeletal muscle.

Industrial Applications of Fats and Oils

The potential for commercial exploitation of fats and oils for industrial applications has also been rated very high not less than their use for food.

1. **Paints**: As drying oils as well as the specialty chemicals.
2. **Cosmetics**: As basic raw material for nail polish, lipstick, creams and lotions.
3. **Polymers**: Epoxides of oils are used as plasticizers applications in the polymer industry.
4. **Energy**: As a base material for biodiesel
5. **Lubricants:** A range of lubricants (biodegradable) based on oils and their derivatives.
6. **Surfactants:** A range of **surfactants** is made from derivatives of fats and oils.

6.7 Detergents

Detergents are the unique substances, which always prefer stay at the interface of the two different phases. The molecular structure of detergents has attributes like two different moieties (polar and non polar) in the same molecule by which one part of the detergent molecule prefers to stay in the polar phase while the other one stays in the non polar phase. This way, a sort of bridge is built between the two different types of phases. It is because of the fact that the detergents are active at interfaces; they are also called as “surfactants”. Surfactants or detergents thus are very useful chemicals because in our day – to-day activities at all levels, we encounter problems associated with the interfaces as also due to the fact that either we need to make two different phases miscible or we need to separate homogeneous and stable systems consisting of different phases. In all such cases, Surfactants or detergents are found useful in negotiating the two different phases for both the stabilization as well as destabilization of the systems.

For example, detergents can act as a link between water and the dirt particles, on any surface like fabrics that need to be cleaned. The detergent molecules can perform this function because one end is hydrophobic. The hydrophilic end is similar in structure to compounds that get hydrated. The hydrophobic part of the molecule frequently consists of a hydrocarbon chain that is similar to the structure of dirt, grease, oil, fat and hydrophobic solids. The net result of this peculiar structure permits detergent to reduce the surface tension of water and dirt to affect cleaning of surfaces.

When detergent is used, the dirt particles on the surfaces detach from the dirty surface and go into the solution of detergent, the earliest known detergents are the soaps which are made from animal and vegetable fats and oils. Chemically, it is the sodium or potassium salt of a fatty acid, formed by the reaction fatty acid group with an alkali.

To start with, Europeans produced soap from the tallow of goats reacting it with beech ash furnishing the alkali. Boiling olive oil with lead oxide produced a sweet tasting substance called glycerin along with the soap. Thus fats did not combine with alkali to form soap but were first decomposed to form fatty acid and glycerol.

In the present times for manufacturing soaps, oils or fats are treated with an aqueous solution of an alkali such as sodium hydroxide- a process called saponification to form glycerin and soap (sodium salt of fatty acid).

Hard soaps are made from oils and fats that contain a high percentage of saturated acids, which are saponified with sodium hydroxide. Soft soaps are semi fluid soaps made from linseed oil, cottonseed oil, and fish oils, which are saponified with potassium hydroxide.

Transparent soaps usually contain castor oil, high-grade coconut oil, and tallow. A fine toilet soap made of high grade olive oil is known as castile soap. Shaving soap is a potassium-sodium soft soap, containing stearic acid, which gives a lasting lather. Shaving cream is a paste that is a combination of shaving soap and coconut oil.

Soap powder is a hydrated mixture of soap and sodium carbonate. Powdered soap, which is used in dispensers, is a dry soap that has been pulverized to a fine powder. Liquid soap is a solution of soft potassium soap dissolved in water.

Here, it may be noted that there are several other types of detergents which have been developed over the years and the dependence on soaps for such applications is minimal.

Chemical structure of Detergents

All the detergents or surfactants have one basic feature in their structure and that is the presence of two moieties of different nature: one being hydrophilic whereas the other one being hydrophobic. Depending upon the nature of the hydrophilic group, the detergents can be nonionic, anionic, cationic, amphoteric. For better understanding, let us discuss the structure of ionic and non-ionic detergents separately. The hydrophobic part is generally a long chain hydrocarbon in the case of most of the detergents. Detergents with the hydrophobic part consisting of the long chain compounds with little affinity for aqueous media. The hydrophilic part is small in size (especially for ionic detergents) but it has a strong affinity for water because either it is charged positively or negatively or it consists of groups with high degree of solvation in water through H-bonding.

Action of Detergents

Once detergent has dissolved in water, its molecules will surround any patch of dirt on fabric, forming a ring around it called a micelle. Detergents have a hydrophilic and a hydrophobic part.

Micelle formation allows the hydrophobic chain to avoid water and hydrophilic head to avoid dirt. Micelle formation makes the dirt soluble in water and thus it helps remove stain from the cloth. Cleaning action is the absorption of dirt and grease into the center of soap micelles, which transforms a stain into a soluble substance that can be, rinsed away.

Types of detergents

A large number of detergents are available for scientific use**.** They are usually categorized according to the type of hydrophilic group they contain- anionic, cationic, amphoteric or nonionic.

There are four main types of detergents.

Anionic detergents

Anion is a negatively charged molecule. The detergency of an anionic detergent is vested in the anion. The anion is neutralized with an alkaline or basic material to produce full detergency.

Anionic detergent can belong to the following groups: -

Alkyl Aryl sulphonates

Linear alkyl benzene suphonates are the largest used detergents in the world, and the alkyl aryl sulphonates as a group would represent more than 40% of all the detergent used. They are cheap to manufacture, very efficient and the petroleum industry is a starting point for the base raw material.

Long chain fatty alcohol sulphates

Made from fatty alcohols, which are sulphated, these are used extensively in laundry detergents. They can be produced with varying carbon chain lengths, but a C12-C18 alcohol sulphate is a good choice. Other groups are the olefinic sulphates and sulphonates, alpha olefin sulphates and sulphonates, sulphated monoglycerides, sulphated ethers, sulphosuccinates, alkane sulphonates, phosphate esters, alkyl is ethionates, sucrose esters.

The anionic detergents are used extensively in most detergent systems, such as dish wash liquids, laundry liquid detergents, laundry powdered detergents, car wash detergents, shampoo's, etc.

Cationic detergents

Cation means positively charged. The detergency is in the Cation which can be a substantially sized molecule. Strong acids are used to produce a Cl^- anion as the "neutralizing agent", although no neutralization takes place in the manufacturing process.

These have poor detergency and can be used as germicides, fabric softeners, and special emulsifiers.

Cationic and anionic detergents cannot be mixed together as it causes precipitation. The cationic detergents invariably contain amino compounds. The most widely used are the quaternary ammonium salts.

Non-ionic detergents

As the name implies, no ionic constituents are present. They are ionically inert. The vast majority of all nonionic detergents are condensation products of ethylene oxide with a hydrophobe. This group of detergents is enormous and the permutations are endless.

Amphoteric detergents

These contain both acidic and basic groups in their molecule, and can act as cationic and anionic detergents, depending on the pH of the solution. These have the characteristics of both anionic and cationic detergent. They tend to work the best at neutral pH and they are found in shampoos, skin cleaners and carpet shampoo. They are very stable in strong acidic conditions and have found favor for use with hydrofluoric acid.

Two properties of detergents are very important in their consideration for biological studies: the critical micelle concentration (CMC) and the micelle molecular weight. The CMC is the concentration at which monomers of detergents join together to form micelles. Each detergent micelle has a characteristic molecular weight. Detergents with a high micelle molecular weight are difficult to remove from samples by dialysis. The CMC and the micelle molecular weight vary depending on the buffer, salt concentration, pH and temperature. Adding salt will lower the CMC and raise the micelle size.

The following detergents have detrimental properties for some procedures:

1. Phenol containing detergents have a high absorbance at 280nm and thus interfere with protein monitoring. They also induce protein at the Lowry protein assay.
2. High micellar molecular weight interferes with gel filtration and they are not easily removed by dialysis.
3. Sodium cholate and sodium deoxycholate are insoluble at pH 7.5. Above an ionic strength of 0.1% SDS they will often crystallize.
4. Ionic detergents interfere with non denaturating electrophoresis and isoelectric focusing. Ionic detergents are very good solubilizing agents, but they tend to denature proteins by destroying the three dimensional structure. Nonionic and mildly ionic detergents are less denaturing and can be often used to solubilize membrane proteins while retaining protein-protein interactions.

Differences between Soaps and Detergents

Both soaps and detergents are used for washing purposes. They form an emulsion with water and oil which washes dirt away. Soaps are made by the action of sodium hydroxide on fats. This process is called hydrolysis or saponification. It gives soap and glycerol (as a by-product). The soaps are sodium salt of fatty acids and are useful only in soft water as they form an insoluble precipitate in hard water. This precipitate consists of calcium and magnesium salts of higher fatty acids. No lather or emulsion is formed and washing is not possible.

Detergents on the other hand are sodium salts of alkyl or aryl sulphonic acids or sulphonates of aliphatic alcohols. Detergents can be used for washing purposes even in hard water, as the calcium salts of sulphonic acids are water-soluble.

Characterization of Detergents

Since detergents exhibit unique properties when dissolved in water, for characterization of detergents, therefore, various characteristics of detergent solution in water are studied. The commonly used methods for characterisation of detergents are as given below:

(a) Cloud point (b) Kraft point (c) Surface tension and interfacial tension

(d) Critical micelle concentration

The details of each of the methods are described here.

Cloud Point

As described above, all the detergents when dissolved in water undergo two basic phenomenon. Adsorption and micellisation, both of them are due to the hydrophobic interactions where in the detergent molecules reorient themselves in such a way that the hydrophilic part remains with the water molecules whereas the hydrophobic part remains away from them. With the increase in concentration of detergent, the aggregation micellisation of molecules begins with all the hydrophobic chains joined together.

The solutions of detergents in water however undergo changes with the rise in temperature. In the case of nonionics, the rise in temperature causes the dehydration of the hydrophile resulting in the precipitation of the detergent manifested as the solution turning cloudy. The temperature at which this change of phase from homogenous and clear solution to hazy and cloudy form takes place is called as the cloud point of the detergent. The cloud point increases with the increase in the number of moles of EO in the nonionic. In other words, one can understand the hydrophilic character of the detergent from the measurement of cloud point. Detergents which don't turn cloudy even on temperature at which water boils are the highly hydrophilic in nature, for example, NP with 30 moles of EO. In such cases, the cloud point is measured by dissolving the detergents in salt solution in water rather than just water. The salts (eg. Nacl, KCl etc.) in water facilitate the dehydration of detergents which otherwise don't turn cloudy on heating. Similarly the detergents which have the cloud point less than the ambient say 30^{o}C, the measurements cannot be done with solution in water. In such cases, the hydro tropic solvent such as butyl diglycol ether, isopropyl alcohol, ethanol etc. cannot used to solubilise the detergent. The solution of detergent in water with solvent is then used for cloud point measurement.

There are large amounts of information in the literature based on which one can easily determine the type of detergent once the cloud point is known. For example, if the hydrophobe is known, one can determine the number of EO moles attached in the detergent from the result of cloud point unlike the nonionics, the anionic detergents exhibit a totally different behavior when their solution in water are heated.

Kraft Point

In the case of anionic detergents, their solution in water when heated exhibit the increase in solubility rather than precipitation. The temperature, at which the solubility increases drastically, is known as its kraft point. Based on the kraft point, not only one can determine the nature of detergent but once can also make the selection of the suitable detergent for a given application. For example, if the formulation of detergent is to be developed for the washing of fabrics the detergent to be selected would have to be based on the temperature of washing. If washing is to be done at ambient, the detergent to be selected will have to have the kraft point much lower than the ambient temperature. Generally, for washings at lower temperatures one would have to opt for nonionics where as for washings at higher temperature, the anionics would be the preferred choice. The Kraft point depends on several factors such as the hydrophobic chain, type of anionic group and the neutralizing cation.

Surface tension or interfacial tension

As the hydrophobic part remains oriented away from the surface of water, the surface tension is lowered. Based on the surface tension Vs concentration pattern, once can make an assessment of the interfacial behaviour of detergents. Those which show very low surface tension are known for high wetting as well as for solubilisation power. Based on the surface tension data, once can design the detergent formulations for a given application involving different phases. Surface tension depends upon the way the detergent molecules stay at surface and that is directly derived from the size, shape and nature of the detergent.

Critical Micelle Concentration

Based on the CMC of detergents, one can make an assessment of the nature of the detergents. For example, nonionics exhibt much lower CMC than the anionics. For applications where one needs to solubilise the hydrophobic substances in water, one will have to look for detergents with extremely low CMC values.

Exercise 6.1

1. What are the industrial Applications of Fats and Oils?
2. What are the types of detergents?
3. What are the commonly used methods for characterization of detergents?

UNIT 8. CHEMICAL FOOD STUFF PROCESSING

UNIT OBJECTIVES

After completing this unit, you should be able to:

- Define fermentation.
- Discribe the different types of fermentation.
- Describe the fermentation process
- **List** the product of fermentation for varios organisms
- Mention the different types of alcohol beverages and alcohol content.
- Outline the steps in the beer making process.
- Compare the difference between alcohol beverages and spirit
- Describe the preparation of spirit
- Discuss the basic steps and precautions necessary to make wine

8.1 INTRODUCTIONS TO FERMENTATION

Activity 8.1 Define fermentation.In Antiquity how did humans introduce yeasts in their bread dough?

The term “fermentation” derives from the Latin work *fevere* meaning “to ferment.” Fermentation is an ancient process dating back thousands of years. When we talk about fermentation, most of us assume that we are referring to the process used to make wine or beer, i.e. production of alcohol by microorganisms; however, fermentation plays a much greater role in our lives. It is hard to imagine yet it's true. A great majority of the foods we eat are fermented. In fact, the fermentation process accounts for a large part of the foods we eat. Sour cream, pickles, vinegar, sour dough, yogurt, sausage, cheese, bread, and sauerkraut have one thing in common: they are all fermented foods or they mimic fermented foods i.e. where humans introduce in the food the chemical products normally produced by microorganisms.

The definition of fermentation is actually very broad and encompasses various phenomena but in each case, has one thing in common - microorganisms introduced in food, voluntarily or not. These microorganisms can be bacteria, yeast or molds but all of them use the sugars in these foods to grow: bacteria, yeast and mold all break down the sugar to extract the energy, but they do it in different ways, with different end products.

Activity 8.2 What types of organisms use fermentation?

This means that there are different types of fermentation.

- Yeast will break sugar down to CO_2 + H_2O in the presence of oxygen, but to alcohol + CO_2 in the absence of oxygen.
- Some bacteria will break sugar down to alcohol, acetic acid (vinegar) and lactic acid (Leuconostoc).
- Other bacteria will break sugar down to acetic acid only (Acetobacter).
- Some will produce lactic acid (Pediococcus or Lactobacillus) to help curdle milk in the cheese making process.
- Other bacteria will break sugar down to CO_2 and compounds that give the food an off-flavor or toxic properties that make it unfit for consumption (Pseudomonas, Klebsiella, Clostridium).

Fermentation is a metabolic process that release energy from a sugar without the use of oxygen. In such cases the microorganism does not need O_2 to grow. For example, yeast will convert sugar to ethanol in the absence of oxygen. Other microorganisms however convert sugars into a variety of compounds that are also of use to humans, such as lactic acid, acetic acid (vinegar), acetone, methanol and glycerol.

Figure 8.1 and Table 8.1 show some of the compounds produced by these microorganisms.

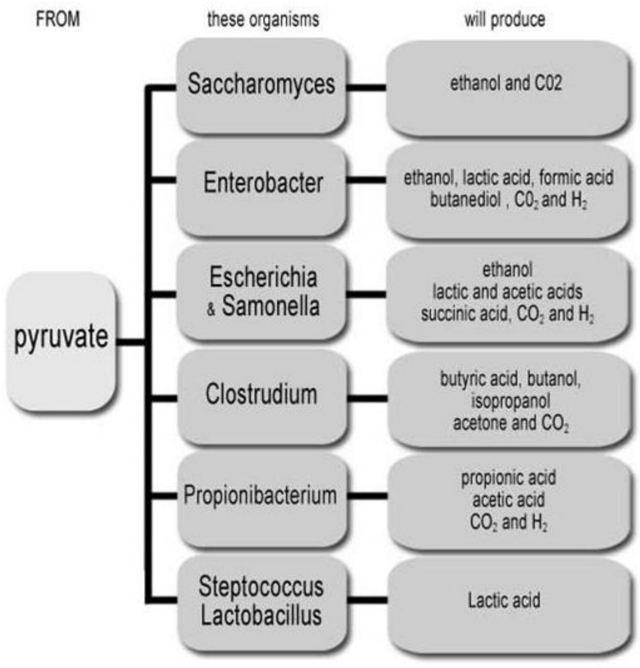
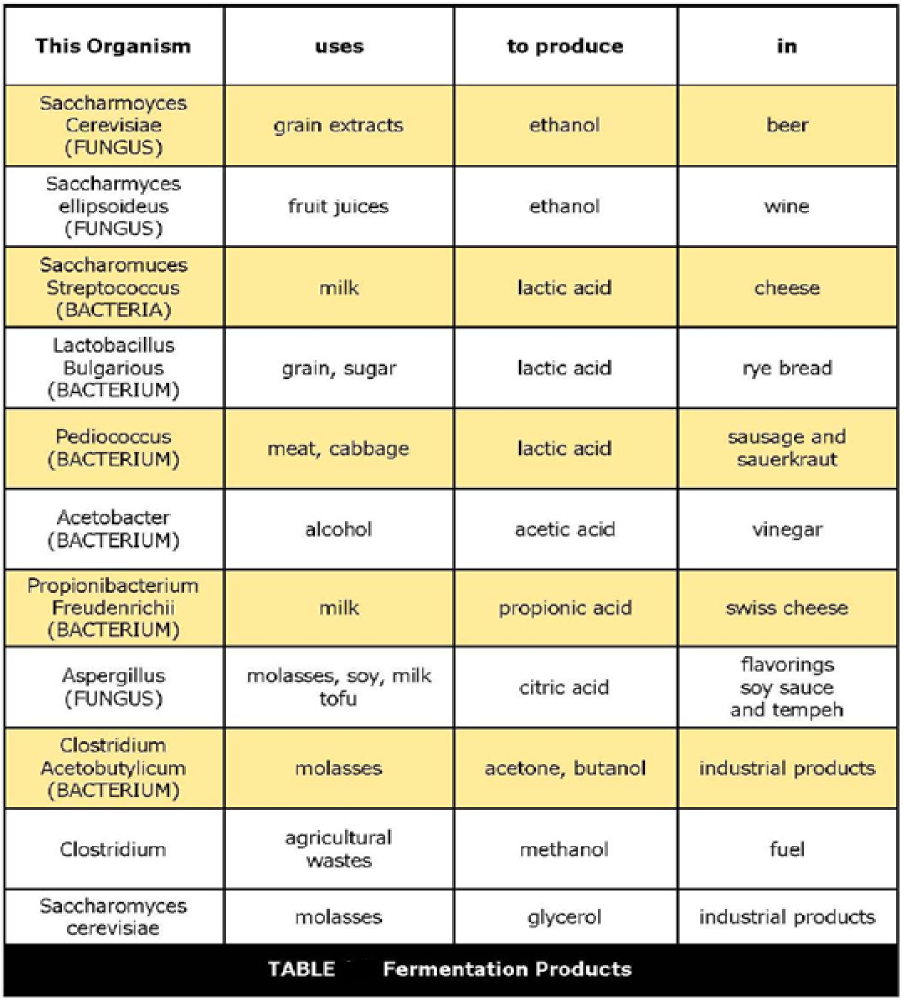


Fig.8.1 the product of fermentation for varios organisms when the starting material is pyruvate



This Organism	uses	to produce	in
Saccharmoyces Cerevisiae (FUNGUS)	grain extracts	ethanol	beer
Saccharmyces ellipsoideus (FUNGUS)	fruit juices	ethanol	wine
Saccharomuces Streptococcus (BACTERIA)	milk	lactic acid	cheese
Lactobacillus Bulgarious (BACTERIUM)	grain, sugar	lactic acid	rye bread
Pediococcus (BACTERIUM)	meat, cabbage	lactic acid	sausage and sauerkraut
Acetobacter (BACTERIUM)	alcohol	acetic acid	vinegar
Propionibacterium Freudenrichii (BACTERIUM)	milk	propionic acid	swiss cheese
Aspergillus (FUNGUS)	molasses, soy, milk tofu	citric acid	flavorings soy sauce and tempeh
Clostridium Acetobutylicum (BACTERIUM)	molasses	acetone, butanol	industrial products
Clostridium	agricultural wastes	methanol	fuel
Saccharomyces cerevisiae	molasses	glycerol	industrial products

TABLE Fermentation Products

Table 8.1. fermentation products

Therefore, we will define fermentation as a process that involves one of the following:

- Alcohol and alcoholic beverages. , - Spoilage of foods by microorganism.

8.2 ALCOHOL BEVERAGES

An alcoholic beverage is a drink containing ethanol.

From ancient times ethanol was used primarily as an alcohol beverage. It is produced through fermentation of carbohydrates (grains, sugars, and starches), the production of alcohol is probably the best known of the fermentation processes.

Fermentation is the process by which alcoholic beverages are manufactured. Alcohol fermentation is used for the industrial production of alcohols and alcoholic beverages. The alcoholic beverage includes the following: Wines, Beer, Whisky,Gin and Liqueurs

Wines are made from a variety of fruits, such as grapes, peaches, plums or apricots. The most common wines are produced from grapes. The soil in which the grapes are grown and the weather conditions in the growing season determine the quality and taste of the grapes which in turn affects the taste and quality of wines. When ripe, the grapes are crushed and fermented in large vats to produce wine.

Beer is also made by the process of fermentation. A liquid mix, called wort, is prepared by combining yeast and malted cereal, such as corn, rye, wheat or barely. Fermentation of this liquid mix produces alcohol and carbon dioxide. The process of fermentation is stopped before it is completed to limit the alcohol content. The alcohol so produced is called beer. It contains 4 to 8 percent of alcohol.

Whisky is made by distilling the fermented juice of cerealgrains such as corn, rye or barley.

Rum is a distilled beverage made from fermented molasses or sugarcane juice and is aged for at least three years. Caramel is sometimes used for colouring.

Brandy is distilled from fermented fruit juices. Brandy is usually aged in oak casks. The colour of brandy comes either from the casks or from caramel that is added.

Gin is a distilled beverage. It is a combination of alcohol, water and various flavours. Gin does not improve with age, so it is not stored in wooden casks.

Liqueurs are made by adding sugar and flavouring such as fruits, herbs or flowers to brandy or to a combination of alcohol and water. Most liqueurs contain 20-65 per cent alcohol. They are usually consumed in small quantities after dinner.

Mead - fermented honey and water, sugar in honey is too concentrated for yeasts to grow so it must be diluted. Probably made by early humans by accident initially. Mead is made now by boiling diluted honey and adding nitrogen containing compounds, then yeast culture. Fermentation process takes 6-8 weeks.

In the preparation of alcoholic beverages several factors have to be considered, such as flavor, taste, appearance, and safety. These require special procedures and standards. The commercial producers of alcoholic beverages each have their own protocols which give their product a distinct taste and flavor, and these are often kept confidential.

Types of alcoholic beverages		
Beverage	**Source**	**Alcohol content (percentage)**
Brandy	Fruit juices	40 - 50
Whisky	Cereal grains	40 - 55
Rum	Molasses/sugarcane	40 - 55
Wines (Port, Sherry,Champagne**,** etc)	Grapes(other fruits)	10 - 22
Beer	Cereals	4 - 8

Table 8.2 type of alcoholic beverages and alcohol content.

The fermentation process starts with one molecule of the six carbon sugar - glucose, and terminates with two molecules of the two carbon alcohol - ethanol, and two molecules of CO_2. The process is as follows:

Sugar (Carbohydrate) ⟶ 2Ethanol + 2Carbon Dioxide

or

$$\underset{\text{glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{ethanol}}{2CH_3CH_2OH} + \underset{\text{carbon dioxide}}{2CO_2}$$

ALCOHOLIC
FERMENTATION

GLUCOSE
↓
PYRUVIC ACID
↓
CO_2
+
ALCOHOL
+
2 ATP

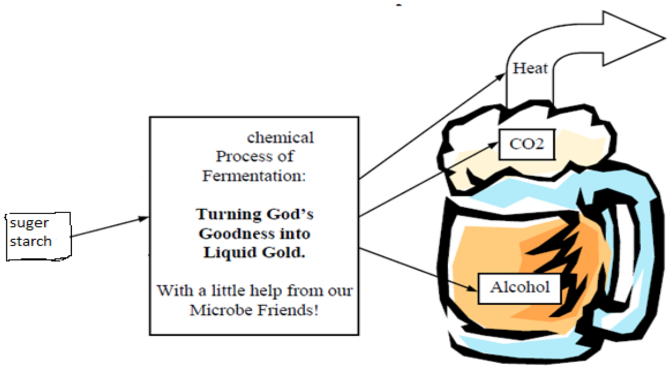


Fig.8.2 Simplified alcohol beverage processes

The fermentation process is not single step but rather there are a series of steps carried out in alcoholic fermentation pathway. It is illustrated below.

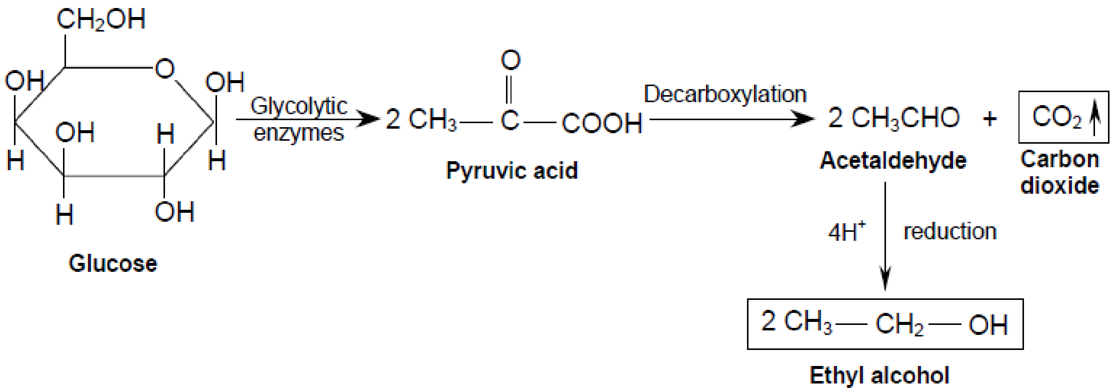


Fig.8.3 Alcoholic fermentation pathway

8.3 MANUFACTURE OF BEER, SPIRIT AND WINE

THE BEER MAKING PROCESS.

1. Malting.

This process will convert the unfermentable starches of the barley into fermentable simple sugars.

Activity 8.3 Why can't yeast cells use starch as a food source?

During grain maturation the sugars made by the plant for storage in the grain (or seed) are "polymerized" into long chains of glucose. That chain is called a starch and is a very efficient way of packaging energy into a minimum space, second only to the energy packaging of fats. Starch cannot provide energy unless it is first broken back down to simple sugars however. The problem is that yeast cannot do that. It lacks the enzymes to do it and can feed only on simple sugars. But when the seed is planted in the ground these enzymes missing in the yeast will be

activated in the seed and will start breaking down the starches to provide the seed with the glucose it needs to generate the energy needed to grow roots and shoots. How can the beer maker fool the seed (or grain) into thinking that it needs to break down these starches? Simply by putting them in water and letting the grain germinate (for a while) (the process is called malting). When enough of these starches have been broken down yeast cells are added and the fermentation can begin. During malting another category of enzymes will contribute to the way beer looks and tastes. These enzymes will degrade proteins in the grain, proteins that form hazes in the fermented product.

The malting process accomplishes three (3) objectives:

- Produce enzymes that degrade starches and proteins.

- make soluble the walls of the endosperm and degrade starches.

- Degrade proteins to supply amino acids to the growing embryo Of course yeast cells take advantage of this food for their own growth needs.

2. Mashing.

During mashing water is added back to the grain in order to allow the enzymes to continue working now that the danger of germination has been eliminated by the kilning.

When water is added again the grain is called the mash grist. Here the composition of the mash may be changed in order to:

a. Maintain the correct acidity. This will keep the enzymes functioning at maximum efficiency.

b. Maintain the correct balance of minerals that will contribute greatly to the activity of the enzymes and to the taste of the beer. The mineral balance of water was perfect for beer making.

A common mineral addition is gypsum or $CaSO4$. Often added to precipitate phosphate ions from solution (as calcium phosphate) and free the three $H+$ associated with the phosphate it lowers the acidity level of basic mash to a constant pH 5.4. We can see here that adding gypsum to a mash that is around pH 6.0 will lower the pH to 5.4. Calcium carbonate can also be added to increase the pH; can you describe how? Do not confuse the two compounds as they have very different effects on the pH of a solution.

A pH of 5.4 is ideal for maximum enzyme activity (Can you explain why?). Now while ions are necessary for proper enzymatic function they also impart a taste to the solution they are in (remember drinking “hard” water, a solution of high concentrations of calcium and magnesium). Too much calcium would give the beer a thin taste. Other ions impart different flavors to beer: magnesium is associated with a sour/bitter flavor, sodium, a sour-saline note and chloride a sweeter note. Further, some ions, such as nitrate, iron, are to be avoided because they are toxic to yeast or they impart strong, undesirable flavors.

3. Lautering

The mash is transferred to a straining (or lautering) vessel which is usually cylindrical with a slotted false bottom two to five centimetres above the true bottom. The liquid extract drains through the false bottom and is run off to the brew kettle. This extract, a sugar solution, is called "wort" but it is not yet beer. Water is "sparged" (or sprayed) though the grains to wash out as

much of the extract as possible. The "spent grains" are removed and sold as cattle feed. The liquid obtained by sparging is the wort. This wort is placed in the brew kettle and boiled for three hours to evaporate water and concentrate flavors.

Activity 8.4

Describe what is your view would be an organoleptically pleasing beer. How can you control the production of organoleptically pleasing compounds?

If money was no object what beer would you choose to drink? Explain

Hops are also added to the boiling wort to give its flavor to the beer. *(Hops or "green gold" come from a climbing plant with male and female flowers; only the female flowers are used. There are various varieties, ranging from very bitter to aromatic. Hops grew naturally in our regions in ancient times, and this plant has been used by brewers since time immemorial. In antiquity, it could be replaced by mixtures of aromatic herbs, in particular rosemary and thyme, which had the same preserving effect as hops but of course gave the resulting beverage a quite different flavour.*

hops are added here to give the flavor that is now characteristic of beer. They give a good balance between flavor and bitterness. After the beer has taken on the flavour of the hops, it would be Separated), The boiling also sterilizes the wort, dissolves added sugar (if necessary) and precipitates proteins that might be left in the wort. Color development also occurs as the wort becomes more concentrated and oxidizes. Steam is used as a source of heat for the boiling sugar can be added here. If enough barley malt has been added to the mash there is no need for more sugar. But sugar is cheaper than malt and thus is substituted for malt to give a lighter color and flavor to the beer for the same alcohol content. This also boosts profits enormously because sugar is cheaper than barley. If too much sugar is added to compensate for too little malt however, the concentration of amino acids for yeast growth can be too low and the result can be a poor fermentation.

4. Fermentation

Activity 8.5 What type of fermentation would you use to make beer for your family? If your first batch turned out well, would you switch to a different system in order to make larger quantities? Explain

a. Yeast selection.

At this point yeast cells are added. We have already said that a choice is made here by the brew master as to the type to be used.

- *S. cerevisiae* - *S. uvarum or carlsbergensis,* mixtures of up to three different strains. The reason for this selection is that the brewer is looking for very specific characteristics in their beer and to obtain pure culture.

b. Fermenting systems

The wort is then moved to the fermenting vessels and yeast, the guarded central mystery of ancient brewer's art, is added. It is the yeast, which is a living, single-cell fungi, that breaks down the sugar in the wort to carbon dioxide and alcohol. It also adds many beer-flavouring components.

5. Maturation and conditioning

a. **Lagers**. Traditionally, after fermentation, lagers are transferred to casks at 2 ^oC for up to nine months (the lagering process). This removes unwanted volatiles created during fermentation as casks are vented periodically. It also clears the lager by flocculation, clears the hazes and finishes the fermentation of residual sugars to provide the beer with carbonation.

b. Ales are conditioned (or aged) more rapidly so that finings must sometimes be added to clear them. Ales are carbonated by the addition of sugar or wort (Kraeusen). Volatiles evaporate quickly because of the high temperatures. After conditioning the ales are stored at -2 ^oC for three days to eliminate the haze and the remaining floating yeast cells. Even so traditional ale is more cloudy than the lager because of the rapidity of the fermentation process which prevents complete precipitation of suspended solids and the fact that more malt was used thus increasing the concentration of protein in solution. Are there other reasons???

c. Today conditioning and maturation of ales and lagers are done chemically or mechanically. Clearing is done by centrifugation and hazes are eliminated with finings or enzymes. Lagering time can be cut down by chemical and mechanical means. Carbonation is done by pumping CO_2 into the beer. So though the beer you buy at the store is called a lager it really is not except in its taste, reminiscent of that of a lager. It would be more accurate to simply call it a "ten-day-beer", the time it now takes to produce it. Interestingly not all large scale beer makers use this process.

6. Filtration

Filtering the beer stabilizes the flavour, and gives beer its polished shine and brilliance. Not all beer is filtered. When tax determination is required by local laws, it is typically done at this stage in a calibrated tank. Filters come in many types. Many use pre-made filtration media such as sheets or candles, while others use a fine powder made of, for example, diatomaceous earth, also called kieselguhr, which is introduced into the beer and recirculated past screens to form a filtration bed.

Filters range from rough filters that remove much of the yeast and any solids (e.g. hops, grain particles) left in the beer, to filters tight enough to strain color and body from the beer.

Normally used filtration ratings are divided into rough, fine and sterile. Rough filtration leaves some cloudiness in the beer, but it is noticeably clearer than unfiltered beer. Fine filtration gives a glass of beer that you could read a newspaper through, with no noticeable cloudiness. Finally, as its name implies, sterile filtration (Pasteurization**)** is fine enough that almost all microorganisms in the beer are removed during the filtration process. In most cases modern factory-made beer is pasteurized before shipping. Pasteurization simply means the use of heat to kill microorganisms.

The manufacturing process is shown in the figure 8.1.

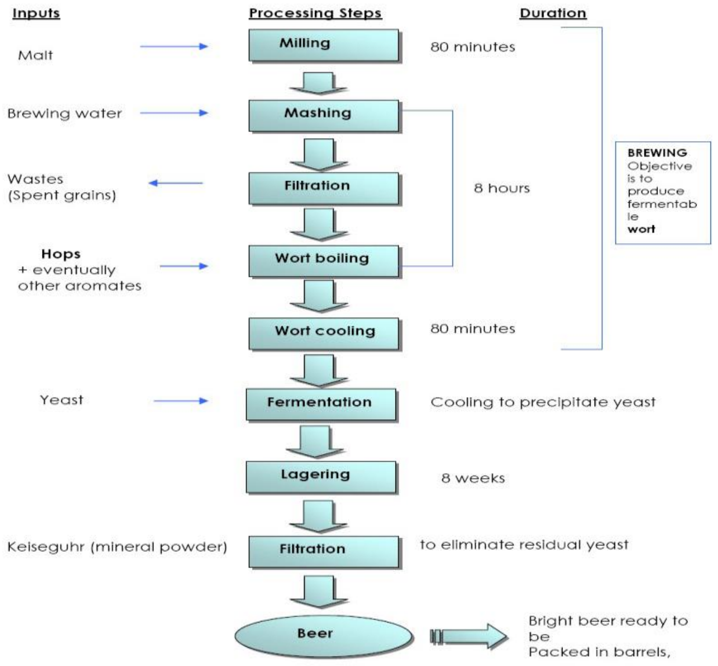


Fig.8.4 the process of beer production

THE SPIRITS MAKING PROCESS.

Alcoholic beverages that have higher alcohol contents.

Beers and wines are limited in their alcohol content by the natural ability of yeasts to resist the poisoning effects this waste product of their own metabolism.

Activity 8.6 What is meant by the term :"concentrating the alcohol by distillation"

However it is possible to obtain alcoholic beverages that have higher alcohol contents. Do you know how it is possible? Processes employed to obtain such high alcohol levels must all be capable of concentrating the alcohol. The process is called **distillation.**

Yeast then ferments this material to provide a solution of between 3 and 12 % alcohol.

This solution is then heated in a process of distillation to evaporate the alcohol preferentially over the water. This increases the alcohol percent to a maximum of 95 % even though most of these beverages are sold at 40% alcohol content. The SPIRITS includes Rum, Whiskey, Bourbon, Vodka, Dry gin, Sour mash, Calvados and Brandy

DISTILLATION

Distillation uses the fact that different liquids boil at different temperatures to separate them from one another. Let us take a mixture of ethanol and water consisting of 5% ethanol. If the temperature of the mixture is raised to 78 °C the ethanol will boil away but not the water. The alcohol vapors can be collected in a cooling column and cooled down to a liquid. The alcohol concentration in the collected liquid is now much higher than in the original solution. At this point only the alcohol has been collected. It is too concentrated for safe consumption The other way is the opposite of boiling it, that is freeze it. As we have said that different liquids have different boiling points, they also have different freezing points. Ethanol freezes at a lower temperature than water. If we freeze a solution of ethanol and water the water on the outside of the container will freeze first and push the ethanol molecules toward the middle. The process will continue until a small volume in the middle of the container has accumulated most of the alcohol, flavor compounds and some water.

THE WINE MANUFACTURING PROCESS

Activity 8.7 What is the strict definition of wine? Compare the alcohol content of wine and brandy.

Wine is very easy to make. It is the result of a very simple process and requires complicated operations only if you are out to make an outstanding wine.

In this chapter we are going to look at the basic steps and precautions necessary to make wine.

Step 1 – Harvesting

Activity 8.8 Is it possible to harvest grape juice that has very high in sugar and low in acid? Explain.

As the grapes ripen the concentration of sugars and aroma compounds rises and the concentration of acids falls. The aim at harvest is to pick the grapes at their optimum composition. This depends on the type of wine to be produced. For example, sparkling wine requires a higher acidity than still table wine. The development of the grapes is followed by taking samples of the grapes at regular intervals from a few weeks before the expected optimum levels will be reached. The samples are analysed for pH (using a pH meter), acid (by titration with sodium hydroxide), sugar (by refractive index or chemical reduction of copper salts) and flavour compounds (by tasting). When optimum levels are reached, the grapes are harvested.

Step 2 - Crushing and destemming

Destemming/crushing equipment removes the grapes from their stems and crushes the fruit to release the juice. The stems are removed as the bunches pass through a perforated rotating cylinder in which the grapes fall through the perforations while the stems are separated out by beathers. The berries are then passed through rollers and crushed.

Today we use a compound called sodium (or potassium) metabisulfite, which combines with water to produce SO_2. Sulphur dioxide (5 - 10% solution of metabisulphite) is usually added to the grape bunches as they are fed into the crusher/destemmer.

The SO_2 inhibits the growth of wild microorganisms and prevents oxidative browning of the juice. Molecular SO_2 is the active biocide, but in solution this is in equilibrium with inactive HSO_3

- At wine pH only 2 - 8% of the SO_2 exists in the molecular form, but this is usually sufficient to give the required protection. Wherever possible during the manufacturing process the juice is kept under a blanket of CO_2 to exclude air, and if necessary more SO_2 is added to maintain the level of molecular SO_2 at a minimum of 80 ppm.

Step 3 - Juice preparation

The free-run juice is separated from the crushed berries, which are pressed by gentle squeezing to obtain a high quality juice. The juice is allowed to settle overnight or is centrifuged to clarify it. If necessary pectolytic enzymes are added to remove haze. Finally, the pulp is then squeezed almost dry. This final juice is of low quality and is used for cask wine or fermented for distillation into alcohol for sherry or port production.

Step 4 – Fermentation

Fermentation is begun by inoculating the juice with the chosen wine yeast. These yeast catalyses a series of reactions that result in the conversion of glucose and fructose to ethanol:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

The driving-force behind this reaction is the release of energy stored in the sugars to make it available to other biological processes. In aerobic conditions, the reaction can proceed further and convert the ethanol to H_2O and CO_2, releasing all of the energy present in the original sugars. This process is undesirable in wine production, so fermentation is usually carried out under a blanket of CO_2 to exclude oxygen and hence maximize alcohol production.

Step 5 – Purification

Activity 8.9 Compare filtered and non-filtered wines.

Proper filtration results in the removal of insoluble solids and removal of microorganisms, assuring a microbiologically stable, bottled product.

Racking

The word simply means to separate the wine from the deposit at the bottom unwanted solids, salts and microorganisms are removed through a variety of physical processes.

Fining

Fining is the last resort if a wine does not clear of its own accord. These hazes can be due to proteins or other small particles that are too small to fall to the bottom and too large to be invisible. Often also large particles are kept from binding to each other (and consequently precipitate) because they both carry negative charges on their surfaces. The charges will repel other particles keeping them from binding. They are called colloids in chemical terms. The haze is due to the fact that when light hits the particle it is deflected because of the size of the particle and so you see less light going through the solution; it thus appears turbid (cloudy) to you.

The fining material will bind these particles into large aggregates that will then deposit at the bottom; we call that coagulation. The best fining agent is gelatin, from your local grocery store. It will bind the colloids that you want to get rid of, and then the wine is bottled and sold. The whole process that summarizes manufacturing of wine (white and red) is outlined in the flow chart below.

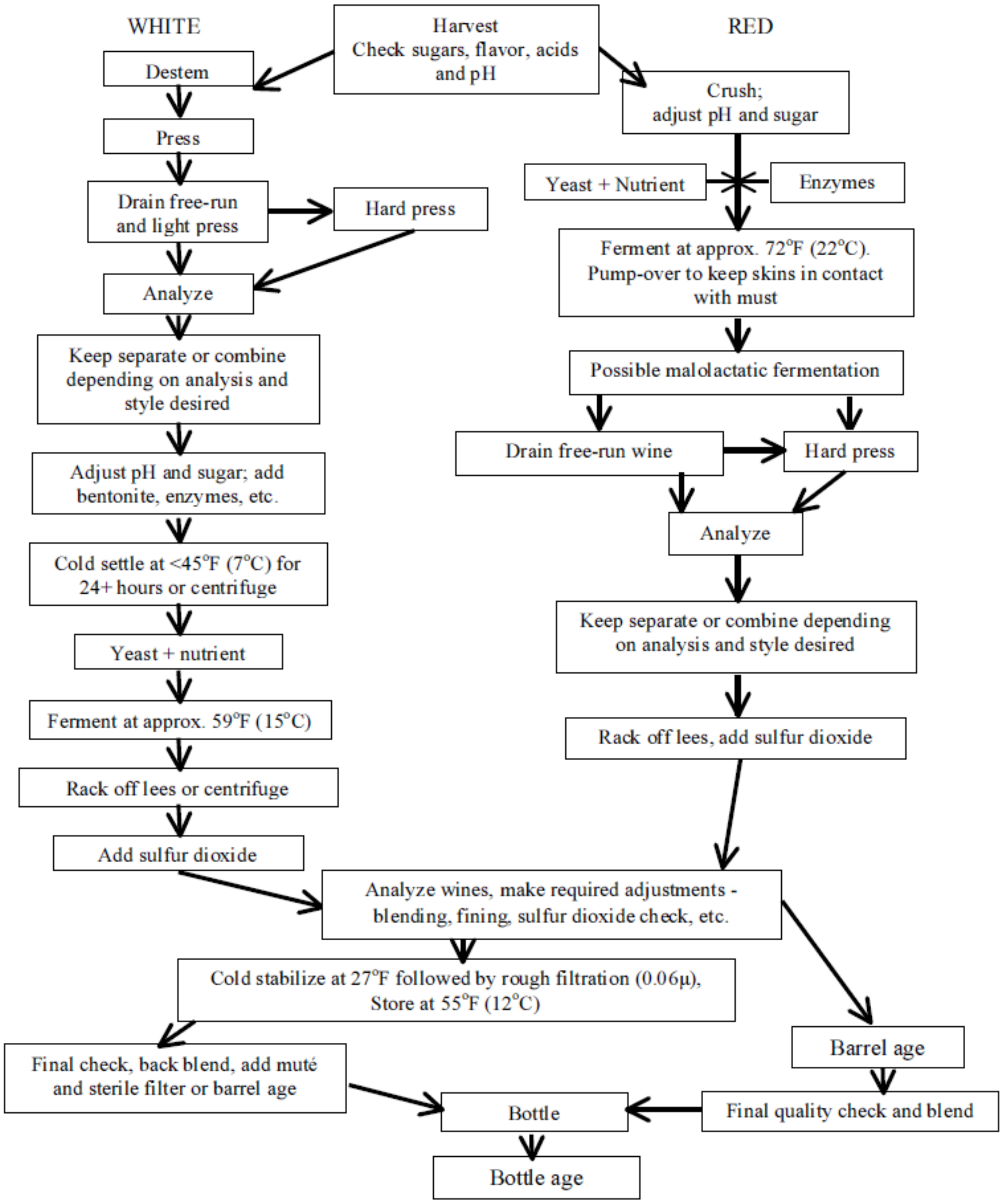


Fig. 8.5 Generic flow charts for processing white and red wine.

Unit Summery

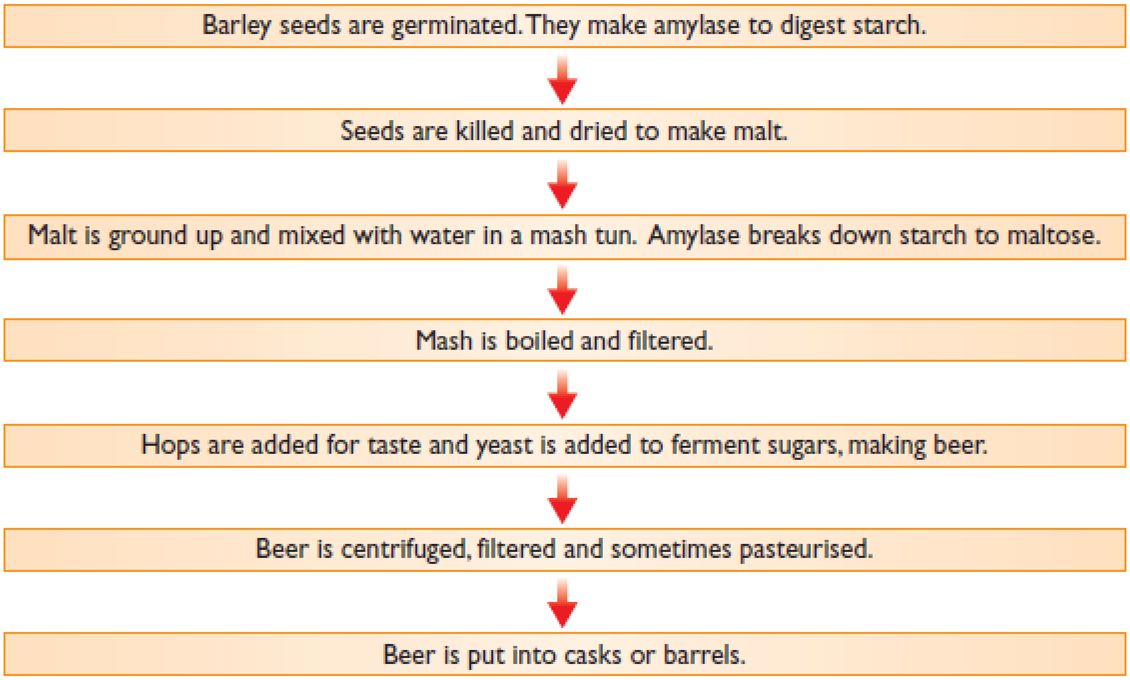
- Fermentation is the process by which alcoholic beverages or acidic diary products (cheeses, yogurt) are manufactured. It is a way for a cell to obtain energy without using oxygen.
- the alcoholic fermentation of glucose is shown in the chemical equation below

$$\underset{\text{glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{ethanol}}{2CH_3CH_2OH} + \underset{\text{carbon dioxide}}{2CO_2}$$

- Fermentation has a wide variety of products. These include:

- Dairy products– Cheese, yogurt
- Beverages– Beer, wine
- Antibiotics
- Chemicals– Citric and acetic acid, amino acids, enzymes, vitamins
- Fuels– Ethanol, methanol, methane

- An alcoholic beverage is a drink containing ethanol. Alcoholic beverage includes the following: Wines, Beer, Whisky,Gin and Liqueurs.
- the process of beer production is summarized below



Barley seeds are germinated. They make amylase to digest starch.

Seeds are killed and dried to make malt.

Malt is ground up and mixed with water in a mash tun. Amylase breaks down starch to maltose.

Mash is boiled and filtered.

Hops are added for taste and yeast is added to ferment sugars, making beer.

Beer is centrifuged, filtered and sometimes pasteurised.

Beer is put into casks or barrels.

- Spirits is an alcoholic beverage that has higher alcohol content. The alcohol is concentrated through distillation. The spirits includes rum, whiskey, bourbon, vodka, dry gin, sour mash, calvados, brandy etc.

- The wine manufacturing process involves: harvesting, crushing, juice preparation, fermentation and purification.

Exercise 8.1

1. Name four majors products of fermentation.
2. Distinguish wort from beer.
3. Why is malting necessary in the beer making process?
4. Explain the principle by which distillation is possible.
5. Why is Racking important in wine making?
6. What are the advantages of using metabisulfite in wine making?

9. PHARMACEUTICALS

UNIT OBJECTIVES

After you have completed this chapter, you should be able to:

- Define drugs
- Describe the use and production of antibiotics
- Mention Examples of antibiotics
- State the production process of penicillin and aspirin
- Write the structure of some of the anti malarial, anti viral and anti bacterial drugs
- Describe the mechanism of action of sulfonamides

The pharmaceutical industry manufactures drugs. The term drug refers to an article intended for use in the diagnosis, cure, alleviation, treatment or prevention of diseases in humans and animals.

In the ancient times a large part of medicinal products used were natural products mostly derived from plants. In subsequent centuries, it was agreed that such products must be pure for effective utilization as pharmaceutical products.

Activity 9.1 Are microorganisms useful in medicine? Explain.

Pharmaceuticals are produced either synthetically or biosynthetically. Fermentation has long been used to manufacture most of the important drug classes such as antibiotics, vitamins and hormones. Micro-organisms growing under controlled fermentation conditions perform complex chemical transformations to produce products more economically than by purely chemical conversions.

The modern pharmaceutical industry traces its origin in the 19th century. This was followed by the emergence of pharmaceutical chemistry and pharmacology as scientific fields at the end of the 19th century. With great emphasis placed on purity of pharmaceutical products, modern pharmaceutical industry devotes much of its effort on the separation and purification of individual products extracted from plants and animals using methods that are sensitive to time, temperature and acidity.

9.1 Antibiotics

Activity 9.2 What are antibiotics?
What is the use of antibiotics? How they are produced?
Name example of antibiotics.

Antibiotics, also known as antimicrobials, are medications that fight bacterial infections.

- ✓ Antibiotics are chemical substances that can inhibit the growth of, or destroy, harmful micro-organisms.
- ✓ They are derived from special microorganisms or other living systems, and are produced on an industrial scale using a fermentation process.
- ✓ The large-scale production of an antibiotic depends on a fermentation process. During fermentation, large amounts of the antibiotic-producing organism are grown.
- ✓ The organisms produce the antibiotic material, which can then be isolated for use as a drug.

Examples of antibiotics, the related microorganisms and therapeutic usages**:**

1. **Amphotericin B** produced by *Streptomyces nodosus used for* deep-seat edmycotic infections
2. **Bacitracin** produced by *Bacillus subtilis* applied topically in ointment form
3. **Chloramphenicol** produced by *Streptomyces ven. zuelae* broad spectrumagent useful in typhoid fever
4. **Erythromycin** produced by *Streptomyces erythreus active against gram* +ve and some Gr –ve organisms
5. **Griseofulvin** produced by antibiotic effective against ringworm.
6. **Neomycin** produced by *Streptomyces fradiae used for* local infections *viz.,*burns, ulcers, wounds, impetigo, infected dermatoses, furunculosis, and conjunctivitis
7. **Oxytetracycline** produced by *Streptomyces rimosus used as* broad spectrum antibiotic
8. **Penicillin** produced by *Penicillium notatum, Penicillium chrysogenum* bactercidal, for most Gram +ve and certain Gram –ve organisms.
9. **Streptomycin** produced by *Streptomyces griseus. used for* treatment of tuberculosis in conjunction with drugs like : isoniazid and rifampicin

Antibiotics are either bactericidal or bacteriostatic. They kill bacteria or inhibit bacterial growth respectively.

Raw Materials required for antibiotic production

Activity 9.3
What raw materials are required for the growth of antibiotics?

- The compounds that make the fermentation broth are the primary raw materials required for antibiotic production.
- Typically, it contains a *carbon source, Nitrogen source*
- Additionally, trace elements needed for the proper growth of the antibiotic producing organisms are included. These are components such as phosphorus, sulfur, magnesium, zinc, iron, and copper introduced through water soluble salts. To prevent foaming during fermentation, *anti-foaming agents* such as *lard oil, octadecanol, and silicones* are used.

The main focus of industrial chemistry is on the manufacturing process. Thus we will see the production of the most common antibiotic drugs.

Penicillin Production Process

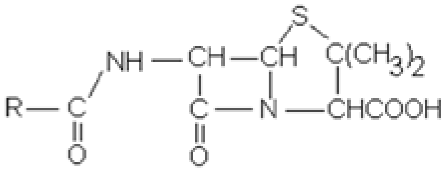


Fig.9.1 structure of penicillin

Spores of P. chrysogenum are used to inoculate 100 ml of growth medium in a 500 ml shake flask. After 4 days incubation, the contents are transferred to growth medium in a 500 L reactor. After three days incubation, this culture is used to inoculate a 180 m^3 reactor. Final Fermentation at about pH 6.5 and 23-28 ^oC is completed in 5-6 days. With good microorganism strains, about 10 % of the carbon in the glucose finds its way into penicillin G whose final concentration may reach almost 30 g/L.

Filtration

The broth contains 20-35 g/L of penicillin. It is pumped to a reservoir tank from where it is fed to a continuous rotary vacuum filter which may use filter aids to form a precoat. The mycelium is separated from the liquor and washed on the filter. It is discharged from the filter as a thick blanket (cake) resembling paper pulp. The penicillin- rich filtrate is chilled to 2-4 ^{o}C to minimize chemical and enzyme degradation during solvent extraction. This operation is necessary since filtration process is not sterile. Growth of bacteria should not be allowed to build in the filtration process because this can result in severe destruction of penicillin by the action of bacterial penicillinases. Therefore, the filter is usually sterilized between runs with steam or germicidal solutions.

Recovery of Penicillin by solvent extraction

This process utilizes the fact that penicillin is preferentially soluble in water or organic solvents depending on whether it is in the free acid or a salt. The filtered and chilled beer (broth) is passed through another filter. Coagulation agents such as aluminium sulphate or tannic acid may be added to precipitate proteinous material. Next, penicillin is extracted with amyl acetate or butyl acetate in a continuous countercurrent process at 0.2-0.4 volumes solvent per volume of beer. Penicillins are strong acids with pKa values in the range of 2.5-3.1. As the acid forms are soluble in many organic solvents, they are extracted with high efficiency into amyl acetate or butyl acetate at pH 2.5-3.0 maintained by addition of phosphoric acid. A water-solvent emulsion is formed. A de-emulsifying agent may be added to break the emulsion. The two phases are separated in a continuous centrifuge. Penicillin is then back extracted into water by the addition of alkali (potassium or sodium hydroxide) or buffer at pH 5.0-7.5 the volume ratio of water to solvent extract in this extractor is 0.1-0.2. After intimate mixing, the two layers are separated. The aqueous phase is chilled. It is then acidified and extracted with an organic solvent such as anhydrous l-propanol, n-butanol or other volatile solvent. Penicillin is once again extracted with water at pH 6.5 – 7.2. An alkaline solution is added to precipitate a salt of the selected base (Na, or K) and the crystals filtered out and freeze-dried. Although the molecular structure of penicillin is known, and it may be synthesized by chemical methods, it is not economic to do so. The production process still relies on fungal fermentation based on biological principles.

9.2 Ant malarial, Anti bacterial and antiviral agents

Anti malarial agents

Malaria is one of the worst sicknesses to affect humankind. Malaria is the commonest cause of fever and morbidity in the tropics and a significant source of mortality, especially among infants and young children.

Malaria is caused by a protozoan, *Plasmodium*, which enters the blood stream as a consequence of a bite by an infected mosquito (*Anopheles*). These female mosquito bite the man for a blood meal which it needs to nourish its eggs, it inoculates the sporozoites into human blood stream, thus spreading the infection. Male mosquitoes do not transmit the disease.

Classification of antimalarial drugs

There are generally three classes of drugs for treating malaria and each is classified according to its therapeutic action against the different life cycle stages of the parasites in human hosts:

(a) Schizonticides (interfere with the growth and multiplication of merozoites),

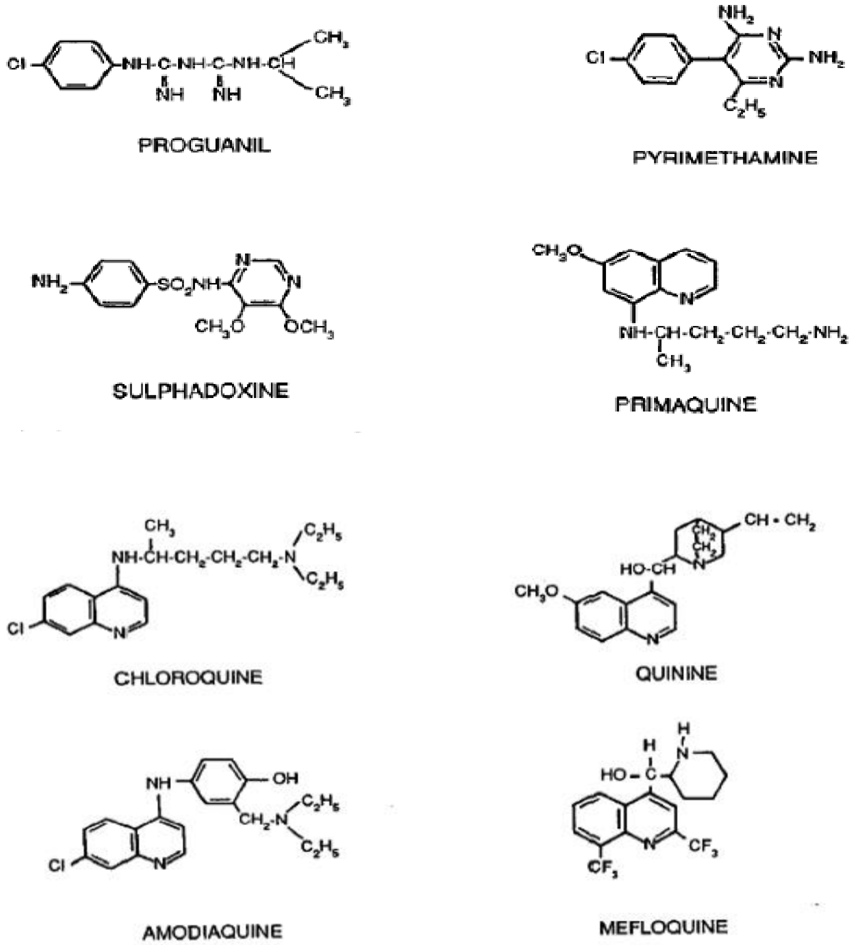
- Exoerythrocytic schizonticides: active against the merozoites in the hepatic or primary tissue schizont, e.g. 8-aminoquinolines are fall into this class;
- Erythrocytic schizonticides: useful against the merozoites in the erythrocytic phase of the life cycle, e.g. quinine and 4-aminoquinolines, 9-aminoacridines are included in this category;

(b) Sporozoitocides (active against sporozoites of parasites), e.g. primaquine, Proguanil etc. They also act against liver schizonts.

(c) Gametocytocides (destroy gametocytes in red blood cells), e.g. chloroquine, artemisinin etc.

Activity 9.4 Can you mention some of the ant malarial drugs commonly sold in the market?

Chemical structure of currently available antimalarial drugs is depicted below



PROGUANIL

PYRIMETHAMINE

SULPHADOXINE

PRIMAQUINE

CHLOROQUINE

QUININE

AMODIAQUINE

MEFLOQUINE

Fig.9.2 structure of some of the ant malarial drugs

Antibacterial agents

The fight against bacterial infection is one of the great success stories of medicinal chemistry.

The success of antibacterial agents owes much to the fact that they can act selectively against bacterial cells rather than animal cells.

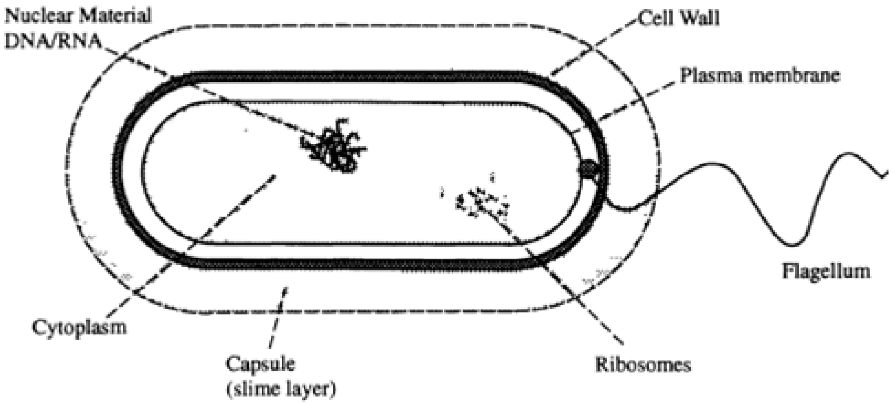


Fig.9.3 the bacteria cell

Mechanisms of antibacterial action

There are four main mechanisms by which antibacterial agents act.

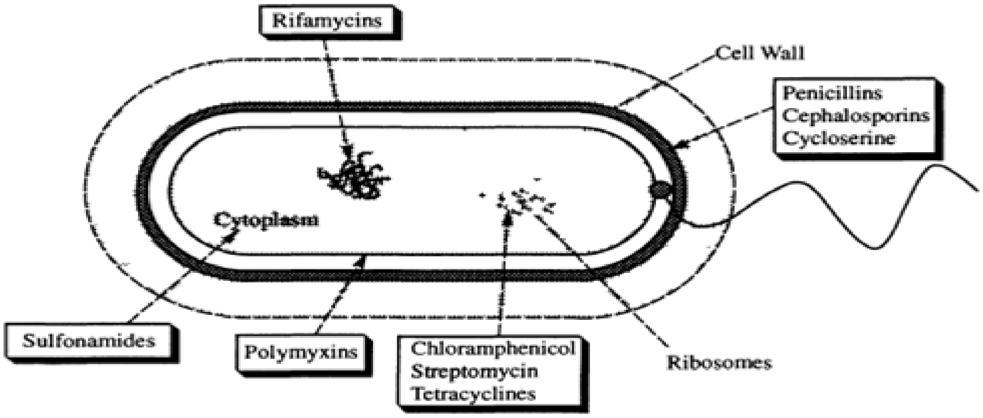


Fig.9.4 Site of anti bacterial action

Activity 9.5 Describe the type of approaches used to treat bacterial diseases

Antibacterial agents which inhibit cell metabolism are called ant metabolites. These compounds inhibit the metabolism of a microorganism, but not the metabolism of the host. They do this by inhibiting an enzyme-catalyzed reaction which is present in the bacterial cell, but not in animal cells. The best known examples of antibacterial agents acting in this way are the sulfonamides.

1. Inhibition of bacterial cell wall synthesis.

Inhibition of cell wall synthesis leads to bacterial cell lysis (bursting) and death. Agents operating in this way include penicillin and cephalosporin. Since animal cells do not have a cell wall, they are unaffected by such agents.

2. Interactions with the plasma membrane.

Some antibacterial agents interact with the plasma membrane of bacterial cells to affect membrane permeability. This has fatal results for the cell. Polymyxins and tyrothricin operate in this way.

3. Disruption of protein synthesis.

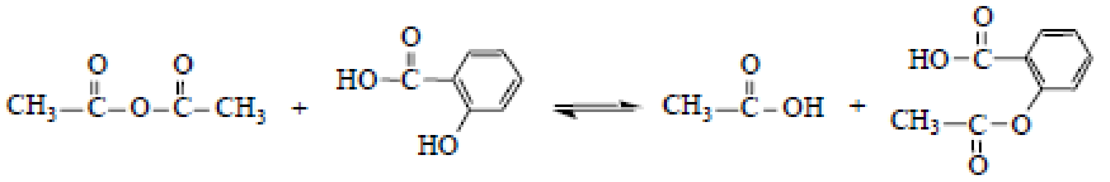
Disruption of protein synthesis means that essential enzymes required for the cell's survival can no longer be made. Agents which disrupt protein synthesis include the rifamycins, aminoglycosides, tetracyclines, and chloramphenicol.

4. Inhibition of nucleic acid transcription and replication.

Inhibition of nucleic acid function prevents cell division and/or the synthesis of essential enzymes. Agents acting in this way include nalidixic acid and proflavin.

Manufacture of Acetylsalicylic acid (Aspirin)

Acetylsalicylic acid, a popular pain-relieving drug (analgesic).It also kills bacteria. The synthesis will start with salicylic acid and make aspirin using acetic anhydride according to the following reaction:



acetic anhydride

salicylic acid ($C_7H_6O_3$)

acetic acid

acetylsalicylic acid (aspirin, $C_9H_8O_4$)

Note that it is the -OH group of salicylic acid that reacts with acetic anhydride to form an ester-like product. The carboxylic acid group of salicylic acid remains unchanged. Phosphoric acid will be used as a catalyst in this experiment.

Having synthesized aspirin, you will purify it by crystallization and filtration. Although there will be some loss of product, good experimental technique will minimize the losses. If your aspirin were going to be used pharmaceutically it would require even further purification.

The main impurity in the crystallized aspirin will be salicylic acid, which will co-precipitate with the aspirin if the procedure is done too quickly.

The first method you will use to determine the purity is the melting point of your product. We will use commercial Mel-temp apparatuses to determine the temperature at which your synthesized crystals melt. If the aspirin is pure, it will melt sharply at the literature value. If it is impure, it will be lower than the literature value by an amount that is roughly proportional to the amount of impurity present.

A more quantitative method of determining the purity of your aspirin is to use absorption spectroscopy. In this method you will react a sample of your purified product with Fe^{3+} (aq), introduced as $Fe(NO_3)_3$. This will form an intensely purple-colored Fe^{3+}-salicylate complex with any remaining salicylic acid impurities, but will not complex with the aspirin. You will use absorption spectroscopy to measure the amount of the complex formed and determine the amount of impurity of your aspirin.

Antiviral agents

Viruses are parasitic, i.e. they utilize:

- ☐ Host metabolic enzymes
- ☐ Host ribosome for protein synthesis

☐ *Structure of viruses*

- ☐ Nucleic acid core: DNA or RNA
- ☐ Often contain crucial virus-specific enzymes
- ☐ Surrounded by protein: “capsid”
- ☐ … and sometimes an outer lipid “envelope”
- ✓ ☐ Often visible by electron microscopy:

HIV-1 Hepatitis B virus Human papillomavirus

Fig.9.5 Electron microscopic structure of different viruses.

❖ *Approaches to treat viral diseases*

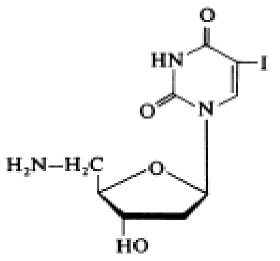
- As viruses are intracellular parasites (utilizing host machinery), there are very few unique targets in viruses. This distinguishes viruses from other infectious organisms:(Bacteria, protozoa, fungi)

❖ Challenges in designing anti-viral treatments:

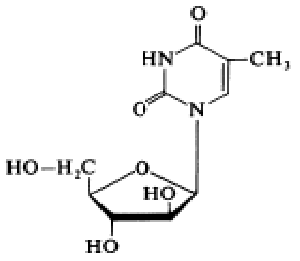
- Host cell must be immune to treatment! (to limit off-target toxicity)
- Viral infection → disease symptoms often associated with latency period

✓ *General anti-viral strategies are to inhibit*:

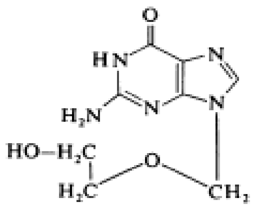
- Viral attachment to host cell, penetration, and un coating
- Viral enzymes:
    - DNA/RNA polymerases, etc
    - Reverse transcriptases, proteases, etc.
- Host expression of viral proteins
- Assembly of viral proteins
- Release of virus from cell surface membranes



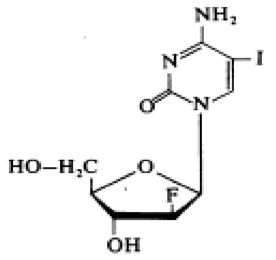
5-Amino-5-iodo-2′,5′-dideoxy-uridine (AI-ddUrd)



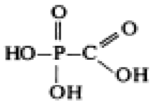
1-*β*-D-Arabinofuranosylthymine (Ara-T)



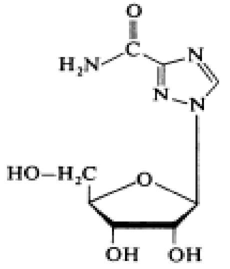
9-(2-Hydroxyethoxymethyl)-guanine acyclovir



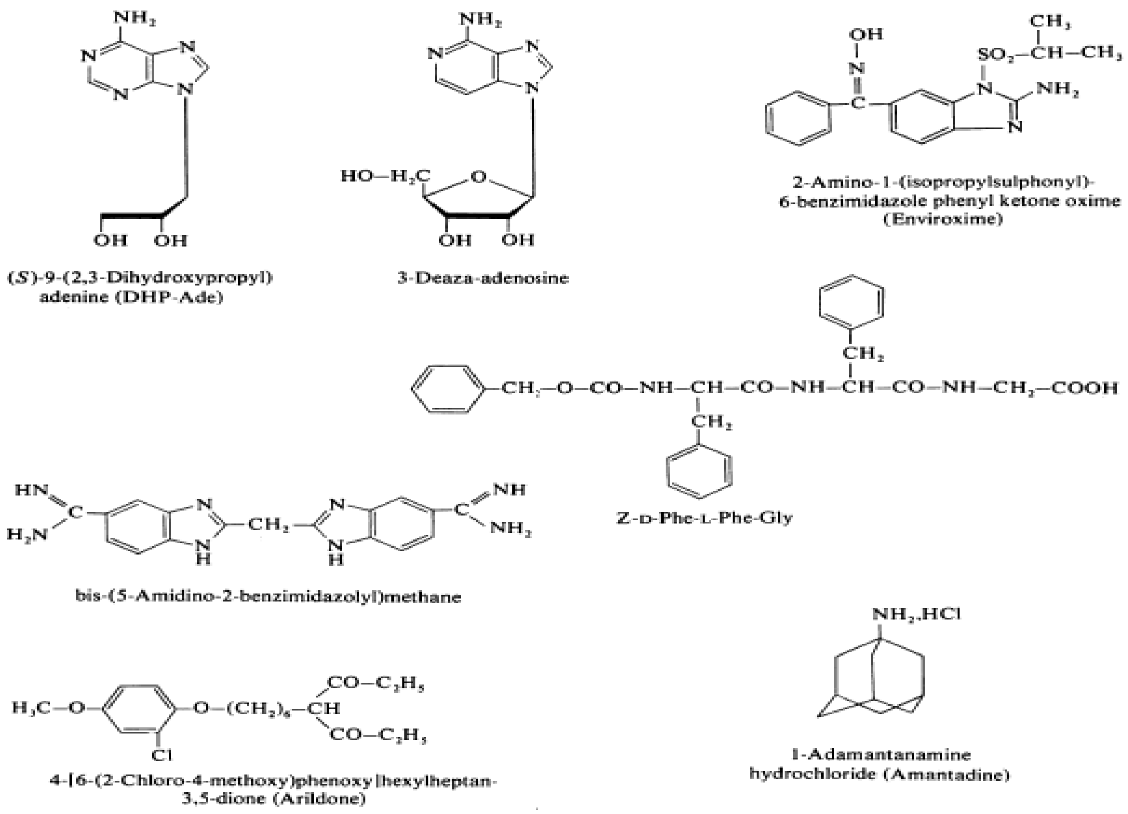
2′-Fluoro-5-iodo-1-*β*-D-arabinofuranosylcytosine (FIAra-C)



Phosphonoformic acid



Ribavirin



(*S*)-9-(2,3-Dihydroxypropyl) adenine (DHP-Ade)

3-Deaza-adenosine

2-Amino-1-(isopropylsulphonyl)-6-benzimidazole phenyl ketone oxime (Enviroxime)

Z-D-Phe-L-Phe-Gly

bis-(5-Amidino-2-benzimidazolyl)methane

4-[6-(2-Chloro-4-methoxy)phenoxy]hexylheptan-3,5-dione (Arildone)

1-Adamantanamine hydrochloride (Amantadine)

Fig.9.6 Structures of and abbreviations for antiviral agents

9.3 Sulfonamide

The best example of antibacterial agents acting as anti metabolites is the sulfonamides (Sometimes called the sulfa drugs).

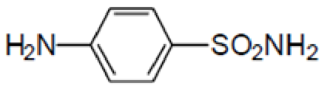


Fig. 9.7 sulfa drug

The sulfa drugs presently have the following applications in medicine:

- treatment of urinary tract infections
- eye lotions
- treatment of infections of mucous membranes
- treatment of gut infections

Mechanism of action

The sulfonamides act as competitive enzyme inhibitors and block the biosynthesis of the vitamin folk acid in bacterial cells. They do this by inhibiting the enzyme responsible for linking together the component parts of folic acid. The consequences of this are disastrous for the cell. Under normal conditions, folic acid is the precursor for tetrahydrofolate—a compound which is crucial to cell biochemistry since it acts as the carrier for one-carbon units, necessary for many biosynthetic pathways. If tetrahydrofolate is no longer synthesized, then any biosynthetic pathway requiring one-carbon fragments is disrupted. The biosynthesis of nucleic acids is particularly disrupted and this leads to the cessation of cell growth and division. Note that sulfonamides do not actively kill bacterial cells. They do, however, prevent the cells dividing and spreading. This gives the body's own defense systems enough time to gather their resources and wipe out the invader. Antibacterial agents which inhibit cell growth are classed as bacteriostatic, whereas agents which can actively kill bacterial cells (e.g. penicillin) are classed as bactericidal.

Sulfonamides act as inhibitors by mimicking p-aminobenzoic acid (PABA) (Fig. 9.9) one of the normal constituents of folic acid. The sulfonamide molecule is similar enough in structure to PABA that the enzyme is fooled into accepting it into its active site. Once it is bound, the sulfonamide prevents PABA from binding. As a result, folic acid is no longer synthesized. Since folic acid is essential to cell growth, the cell will stop dividing.

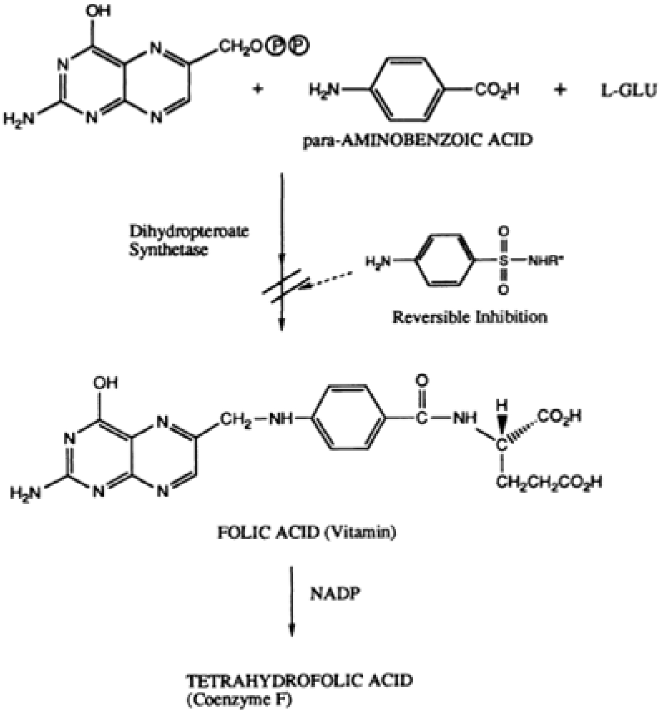


Fig.9.8 mechanism of action of sulfonamides

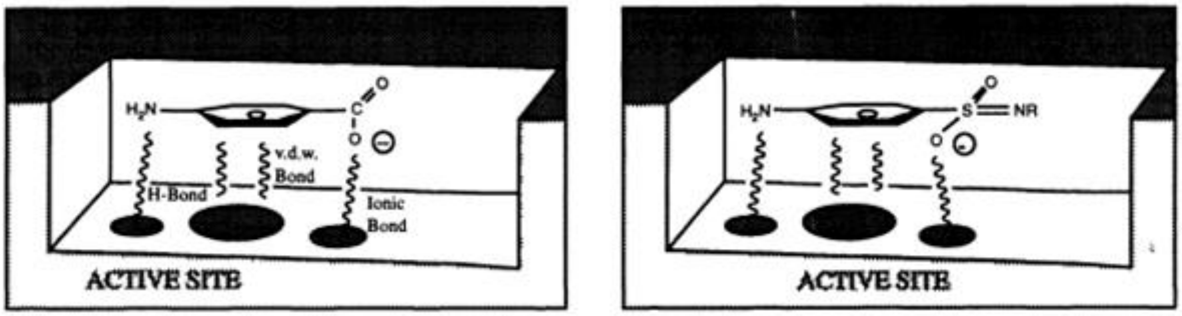


Fig.9.9 Sulfonamide prevents PABA from binding by mimicking PABA.

The manufacture of sulph drugs can be easily synthesized starting from sulfonyl chloride.

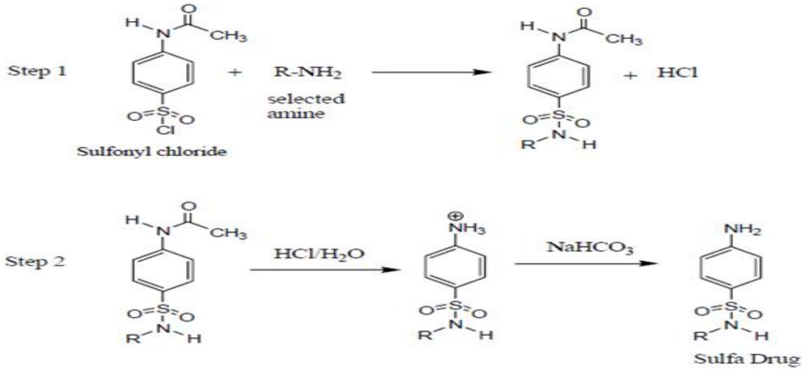


Fig.10 Reaction scheme for the sulfa drug synthesis.

One must be provided with clear evidence from IR, MP and NMR that you synthesized and purified the targeted sulfa drugs.

Exercise 9.1

1. What do you mean by the term bactericidal or bacteriostatic?
2. State the mechanisms by which anti malarial and anti bacterial agents act.
3. Write chemical reaction of synthesis of aspirin.

10. CHEMICALS FOR AGRICULTURE

UNIT OBJECTIVES

At the end of this unit, the learner should be able to:

- list the different types of pesticides
- understand the environmental and health effects of pesticides
- explain the alternatives to extended use of pesticides
- give examples for different classes of insecticides
- mention the characteristics and health effects of organochlorine, organophosphorus and carbamate insecticides.
- discuss the applications and action of fungicides
- describe the different possible classes of herbicides

10.1. INTRODUCTION TO PESTICIDES

Activity 10.1 What are pesticides? What is their advantage? What is their disadvantage?

Pesticides refer to any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. The term includes substances intended for use as a plant growth regulator, defoliant, desiccant or agent for thinning fruit or preventing the premature fall of fruit. Also used as substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport.

Classes of pesticides include: herbicides, insecticides, fungicides, rodenticides, pediculicides, and biocides. Pesticides can also be classified by target organism, chemical structure, and physical state. Pesticides can also be classed as inorganic, synthetic, or biologicals (biopesticides), although the distinction can sometimes be blurred. Biopesticides include microbial pesticides and biochemical pesticides. Plant-derived pesticides, or "botanicals", have been developing quickly. These include the pyrethroids, rotenoids, nicotinoids, and a fourth group that includes strychnine and scilliroside. Many pesticides can be grouped into chemical families. Prominent insecticide families include organochlorines, organophosphates, and carbamates. Organochlorine hydrocarbons (e.g. DDT) could be separated into dichlorodiphenylethanes, cyclodiene compounds, and other related compounds. They operate by disrupting the sodium/potassium balance of the nerve fiber, forcing the nerve to transmit continuously. Their toxicities vary greatly, but they have been phased out because of their persistence and potential to bioaccumulate. Organophosphate and carbamates largely replaced organochlorines. Both operate through inhibiting the enzyme acetylcholinesterase, allowing acetylcholine to transfer nerve impulses indefinitely and causing a variety of symptoms such as weakness or paralysis. Organophosphates are quite toxic to vertebrates, and have in some cases been replaced by less toxic carbamates. Thiocarbamate and dithiocarbamates are subclasses of carbamates. Prominent families of herbicides include phenoxy and benzoic acid herbicides (e.g. 2,4-D), triazines (e.g. atrazine), ureas (e.g. diuron), and Chloroacetanilides (e.g. alachlor). Phenoxy compounds tend to selectively kill broadleaved weeds rather than grasses. The phenoxy and benzoic acid herbicides function similar to plant growth hormones, and grow cells without normal cell division, crushing the plants nutrient transport system. Triazines interfere with photosynthesis. Many commonly used pesticides are not included in these families, including glyphosate.

Pesticides can be classified based upon their biological mechanism, function or application method. Most pesticides work by poisoning pests. A systemic pesticide moves inside a plant following absorption by the plant. With insecticides and most fungicides, this movement is usually upward (through the xylem) and outward. Increased efficiency may be a result. Systemic insecticides, which poison pollen and nectar in the flowers may kill bees and other needed pollinators. In 2009, the development of a new class of fungicides called paldoxins was announced. These work by taking advantage of natural defense chemicals released by plants called phytoalexins, which fungi then detoxify using enzymes. The paldoxins inhibit the fungi's detoxification enzymes. They are believed to be safer and greener.

Health and environmental concerns

The **environmental impact of** pesticides is often greater than what is intended by those who use them. Pesticides may cause acute and delayed health effects in those who are exposed. Pesticide exposure can cause a variety of adverse health effects. These effects can range from simple irritation of the skin and eyes to more severe effects such as affecting the nervous system, mimicking hormones causing reproductive problems, and also causing cancer. Strong evidence exists for other negative outcomes from pesticide exposure including neurological, birth defects, fetal death, and neuro-developmental disorder.

Pesticide use raises a number of environmental concerns. Over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species, including non-target species, air, water and soil. Pesticide drift occurs when pesticides suspended in the air as particles are carried by wind to other areas, potentially contaminating them. Pesticides are one of the causes of water pollution, and some pesticides are persistent organic pollutants and contribute to soil contamination. In addition, pesticide use reduces biodiversity, reduces nitrogen fixation, contributes to pollinator decline, destroys habitat (especially for birds), and threatens endangered species. Pests can develop a resistance to the pesticide (pesticide resistance), necessitating a new pesticide. Alternatively a greater dose of the pesticide can be used to counteract the resistance, although this will cause a worsening of the ambient pollution problem.

Alternatives: Alternatives to pesticides are available and include methods of cultivation, use of biological pest controls (such as pheromones and microbial pesticides), genetic engineering, and methods of interfering with insect breeding. Application of composted yard waste has also been used as a way of controlling pests. These methods are becoming increasingly popular and often are safer than traditional chemical pesticides. In addition, EPA is registering reduced-risk conventional pesticides in increasing numbers. Cultivation practices include polyculture (growing multiple types of plants), crop rotation, planting crops in areas where the pests that damage them do not live, timing planting according to when pests will be least problematic, and use of tap crops that attract pests away from the real crop. Release of other organisms that fight the pest is another example of an alternative to pesticide use. These organisms can include natural predators or parasites of the pests. Based on entomopathogenic fungi, bacteria and viruses cause disease in the pest species can also be used.

Interfering with insects' reproduction can be accomplished by sterilizing males of the target species and releasing them, so that they mate with females but do not produce offspring. This technique was first used on the screwworm fly in 1958 and has since been used with the med fly, the tsetse fly, and the gypsy moth. However, this can be a costly, time consuming approach that only works on some types of insects. Another alternative to pesticides is the thermal treatment of soil through steam. Soil steaming kills pest and increases soil health.

10.2. INSECTICIDES

Activity 10.2 What is pesticide bioaccumulation? How does it differ from biomagnification? Explain with examples.

Insecticides are chemicals that kill insects. Chemical insecticides are divided into two main groups:

I. **Organic insecticides:** organic insecticides are classified into three groups:
   a) Organochlorine compounds

b) Organophosphorous compounds
c) Carbamates

Organochlorine compounds: these compounds are chlorinated hydrocarbons. They are referred to as organochlorines. Some of their common characteristics are:
They are broad spectrum i.e. they kill large number of insects, are very persistent i.e. they can stay in environment for a long time with out degradation, are chemically stable and have low solubility in water.

DDT and BHC are among the most common organochlorine insecticides.

DDT (Dichlorodiphenyltrichloroethane): an organochlorine insecticide which is a white crystalline solid, tasteless and almost odorless. Technical DDT has been formulated in almost every conceivable form including solutions in xylene or petroleum distillates, emulsifiable concentrates, water-wetable powders, granules, aerosols, smoke candles, and charges for vaporizers and lotions. DDT is similar in structure to the insecticide methoxychlor and the acaricide dicofol. It is a highly hydrophobic, nearly insoluble in water but has a good solubility in most organic solvents, fats, and oils. DDT does not occur naturally, but is produced by the reaction of chloral (CCl_3CHO) with chlorobenzene (C_6H_5Cl) in the presence of sulfuric acid, which acts as a catalyst. In insects it opens sodium ion channels in neurons, causing them to fire spontaneously, which leads to spasms and eventual death. Insects with certain mutations in their sodium channel gene are resistant to DDT and other similar insecticides. DDT resistance is also conferred by up-regulation of genes expressing cytochrome P450 in some insect species.In humans; however, it may affect health through genotoxicity or endocrine disruption.

DDT is a persistent organic pollutant that is extremely hydrophobic and strongly absorbed by soil. Depending on conditions, its soil half life can range from 22 days to 30 years. Routes of loss and degradation include runoff, volatilization, photolysis and aerobic and anaerobic biodegradation. When applied to aquatic ecosystems it is quickly absorbed by organisms and by soil or it evaporates, leaving little DDT dissolved in the water itself. Its breakdown products and metabolites are also highly persistent and have similar chemical and physical properties. DDT and its breakdown products are transported from warmer regions of the world to the Arctic by the phenomenon of global distillation, where they then accumulate in the region's food web. Because of its lipophilic properties, DDT has a high potential to bioaccumulate, especially in predatory birds.

BHC (Benzenehexachoride, gammaxane or Lindane): an organochlorine chemical variant of hexachlorocyclohexane that has been used both as an agricultural insecticide and as a pharmaceutical treatment for lice and scabies. Lindane is a neurotoxin that interferes with GABA neurotransmitter function by interacting with the GABA receptor-chloride channel complex at the picrotoxin binding site. In humans, lindane affects the nervous system, liver and kidneys, and may be a carcinogen. It is unclear whether lindane is an endocrine disruptor.

Organophosphorous compounds:

Organophosphates are quite toxic to vertebrates, and have in some cases been replaced by less toxic carbamates. Commonly used Organophosphorous insecticides include: Malathion, Parathion (also called parathion-ethyl or diethyl parathion. It is a potent insecticide and acaricide. It was originally developed by IG Farben in the 1940s. It is highly toxic to non-target organisms, including humans. Its use is banned or restricted in many countries) and TEPP (Tetraethyl pyrophosphate).

Carbamates:

These are the third group of organic insecticides. They have the general formula $\mathbf{R_1OCONHR_2}$**.** Like the organophosphate insecticides, they operate through inhibiting the enzyme acetylcholinesterase, allowing acetylcholine to transfer nerve impulses indefinitely and causing a variety of symptoms such as weakness or paralysis.Examples of carbamte insecticides are: Cabaryl or seiven, Pirimicarb and methiocarb.

II. Inorganic insecticides

The most important inorganic insecticides are: Hydrogen cyanide, Sulfur dioxide, Ethylene oxide, Methyl bromide, Carbon disulfide and Phosphine

Naturally occurring insecticides: Some materials produced by plants are used to kill insects. Some examples are: nicotine, pyrethrum Rotenone, etc.

10.3. FUNGICIDES

Fungicides are chemical compounds or biological organisms used to kill or inhibit fungi or fungal spores. Fungi can cause serious damage in agriculture, resulting in critical losses of yield, quality and profit. Fungicides are used both in agriculture and to fight fungal infections in animals. Chemicals used to control oomycetes, which are not fungi, are also referred to as fungicides as oomycetes use the same mechanisms as fungi to infect plants. Fungicides can either be contact, translaminar or systemic. Contact fungicides are not taken up into the plant tissue, and only protect the plant where the spray is deposited; translaminar fungicides redistribute the fungicide from the upper, sprayed leaf surface to the lower, unsprayed surface; systemic fungicides are taken up & redistributed through the xylem vessels to the upper parts of the plant. New leaf growth is protected for a short period. Most fungicides that can be bought retail are sold in a liquid form. A very common active ingredient is sulfur, present at 0.08% in weaker concentrates, and as high as 0.5% for more potent fungicides. Fungicides in powdered form are usually around 90% sulfur and are very toxic. Other active ingredients in fungicides include neem oil, rosemary oil, jojoba oil, the bacterium *Bacillus subtilis*, and the beneficial fungus *Ulocladium oudemansii*.

Fungicide residues have been found on food for human consumption, mostly from post-harvest treatments. Some fungicides are dangerous to human health, such as vinclozolin, which has now been removed from use.

10.4. HERBICIDES

Herbicides, also commonly known as **weed killers**, are pesticides used to kill unwanted plants. Selective herbicides kill specific targets while leaving the desired crop relatively unharmed. Some of these act by interfering with the growth of the weed and are often synthetic "imitations" of plant hormones. Herbicides used to clear waste ground, industrial sites, railways and railway embankments are non-selective and kill all plant material with which they come into contact. Smaller quantities are used in forestry, pasture systems, and management of areas set aside as wildlife habitat.

Depending on their nature, herbicides are classified in to the following types.

A. **Inorganic herbicides** such as Ammonium sulphamate($NH_4SO_3.NH_2$),Sodium chlorate($NaClO_3$), Borax ($Na_2B_4O_7.10H_2O$) Ferrous sulphate ($FeSO_4$) and Calomel, Hg_2Cl_2

Typical herbicides commonly used contains 40% Sodium chlorate, $NaClO_3$, 50% sodium metaborate, $NaBO_2$, and 10% inert filter. These herbicides are non-selective and must be used with considerable care in protecting the desired plants.

B. **Organic herbicides:** The first widely used organic herbicide was 2,4-dichlorophenoxyacetic acid, often abbreviated 2,4-D. It was first commercialized by the paint company Sherwin-Williams and saw use in the late 1940s. It is easy and inexpensive to manufacture, and kills many broadleaf plants while leaving grasses largely unaffected, although high doses of 2,4-D at crucial growth periods can harm grass crops such as maize or cereals. The low cost of 2,4-D has led to continued usage today and it remains one of the most commonly used herbicides in the world. Like other acid herbicides, current formulations utilize either an amine salt (often trimethylamine) or one of many esters of the parent compound. These are easier to handle than the acid**. 2,4-D** exhibits relatively good *selectivity*, meaning, in this case, that it controls a wide number of broadleaf weeds while causing little to no injury to grass crops at normal use rates. An herbicide is termed selective if it affects only certain types of plants, and non-selective if it inhibits a very broad range of plant types. Other herbicides have been more recently developed that achieve higher levels of selectivity than 2,4-D.

2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) was a widely used broadleaf herbicide until being phased out starting in the late 1970s. While 2,4,5-T itself is of only moderate toxicity, the manufacturing process for 2,4,5-T contaminates this chemical with trace amounts of 2,3,7,8-tetrachlorodibenzo-p-dioxin(TCDD). TCDD is extremely toxic to humans. With proper temperature control during production of 2,4,5-T, TCDD levels can be held to about .005 ppm. Before the TCDD risk was well understood, early production facilities lacked proper temperature controls. Individual batches tested later were found to have as much as 60 ppm of TCDD. 2,4,5-T was withdrawn from use in the USA in 1983, at a time of heightened public sensitivity about chemical hazards in the environment. Public concern about dioxins was high, and production and use of other (non-herbicide) chemicals potentially containing TCDD contamination was also withdrawn. These included pentachlorophenol (a wood preservative) and PCBs (mainly used as stabilizing agents in transformer oil). Some feel that the 2,4,5-T withdrawal was not based on sound science. 2,4,5-T has since largely been replaced by dicamba and triclopyr.

Agent Orange was an herbicide blend used by the U.S. military in Vietnam between January 1965 and April 1970 as a defoliant. It was a 50/50 mixture of the *n*-butyl esters of 2,4,5-T and 2,4-D. Because of TCDD contamination in the 2,4,5-T component, it has been blamed for serious illnesses in many veterans and Vietnamese people who were exposed to it. However, research on populations exposed to its dioxin contaminant has been inconsistent and inconclusive. Agent Orange often had much higher levels of TCDD than 2,4,5-T used in the US. The name *Agent Orange* is derived from the orange color-coded stripe used by the Army on barrels containing the product. It is worth noting that there were other blends of synthetic auxins at the time of the Vietnam War whose containers were recognized by their colors, such as Agent Purple and Agent Pink

Some plants produce **natural herbicides**, such as the genus *Juglans* (walnuts, or the tree of heaven; such action of natural herbicides, and other related chemical interactions, is called allelopathy.

10.5. PESTICIDE POLLUTION

It is almost impossible to limit the area of effect of pesticides. Even when it is applied in a very small area, it spreads in the air, is absorbed in the soil or dissolves in the water and eventually reaches a much bigger area. Pesticides also often seep into ground water which we humans consume, poisoning us over time. In addition to these, residual pesticides on the plants are sometimes consumed by animals and even humans leading to very serious illnesses such as cancer and even death.

EXERCISES 10.1

1. **Chlorinated hydrocarbons such as DDT**

a) are noteworthy because of their persistence in the environment
b) are carbamate insecticides developed in 1970 to combat malaria?
c) break down fairly rapidly and pose little risk to the ecosystem
d) are rarely biomagnified in the food chain

2. First generation pesticides refer to

a) Chemicals that affect the early larval stage development of insects
b) Synthetic organic chemicals used for control of pests since world war I
c) Pretreatment compounds applied to crops to enhance effectiveness of later insecticide treatments
d) Various inorganic chemicals such as sulfur, cyanide and heavy metals

3. when a pesticide is used repeatedly over a period of several years, it gradually loses its effectiveness in killing pests. The best explanation for this is

a) Insect species learn to avoid areas where pesticides have been applied
b) Genetically resistance members of pest species survive and reproduce a population that is more resistant to pests
c) Any chemical loses its potency after a time due to breakdown of molecules
d) Insects gradually become immune to effects of the pesticide as humans become immune by vaccination against a disease

4. Relatively new insecticides that have both low persistence and low toxicity to mammals are

a) triazines b) pyrethroids c) organophosphates d) cabamates

5. In lake polluted with a polychlorinated pesticide, which one of the following will contain the maximum amount of the pesticide?

a) small fish b) microscopic animals c) big fish d) water birds

11. DYESTUFFS

UNIT OBJECTIVES

After completing this unit, the student should be able to:

- **compare and contrast natural dyes to synthetic dyes**
- **understand the classes of dyes**
- **explain the chemical constitution of dyes**
- **describe the methods of dyeing**
- **mention the different classes of dyes**

11.1. INTRODUCTION TO DYES

Activity 11.1 What is color fastness? What causes colour?

Today, dyeing is a complex, specialized science. Nearly all dyestuffs are now produced from synthetic compounds. This means that costs have been greatly reduced and certain application and wear characteristics have been greatly enhanced. But many practitioners of the craft of natural dying (i.e. using naturally occurring sources of dye) maintain that natural dyes have a far superior aesthetic quality which is much more pleasing to the eye. On the other hand, many commercial practitioners feel that natural dyes are non-viable on grounds of both quality and economics. In the West, natural dyeing is now practiced only as a handcraft, synthetic dyes being used in all commercial applications. Some craft spinners, weavers, and knitters use natural dyes as a particular feature of their work.

In many of the world's developing countries, however, natural dyes can offer not only a rich and varied source of dyestuff, but also the possibility of an income through sustainable harvest and sale of these dye plants. Many dyes are available from tree waste or can be easily grown in market gardens. In areas where synthetic dyes, mordants (fixatives) and other additives are imported and therefore relatively expensive, natural dyes can offer an attractive alternative.

Natural dyes can be used on most types of material or fiber but the level of success in terms of fastness and clarity of colour varies considerably. Users of natural dyes, however, tend to also use natural fibers. Natural fibers come mainly from two distinct origins, animal origin or vegetable origin. Fibers from an animal origin include wool, silk, mohair and alpaca, as well as some others which are less well known. All animal fibers are based on proteins. Natural dyes have a strong affinity to fibers of animal origin, especially wool, silk and mohair and the results with these fibers are usually good. Fibers of plant origin include cotton, flax or linen, ramie, jute, hemp and many others. Plant fibers have cellulose as their basic ingredient. Natural dyeing of certain plant based textiles can be less successful than their animal equivalent. Different mordanting techniques are called for with each category. When a blend of fiber of both animal and plant origin is being dyed, then a recipe should be chosen which will accentuate the fiber which is required to be dominant.

A number of plants and minerals yield a suitable mordant, but their availability will be dependent upon your surroundings. Some common substitutes for a selection of mordants are listed below.

- Some plants, such as mosses and tea, contain a small amount of aluminium. This can be used as substitute to alum. It is difficult to know, however, how much aluminium will be present and experimentation may be necessary.
- Iron water can be used as a substitute to ferrous sulphate. This can be made simply by adding some rusty nails and a cupful of vinegar to a bucket-full of water and allowing the mixture to sit for a couple of weeks.
- Oak galls or sumach leaves can be used as substitutes to tannic acid.
- Rhubarb leaves contain oxalic acid.

11.2. COLOUR AND CONSTITUTION OF DYES

Activity 11.2 What are chromophores? Give some examples

Since the discovery of the first synthetic dye in the mid-19th century, chemists have been intrigued by the relationship between the colour of a dye and its molecular structure. Since these early days, the subject has been of special academic interest to those fascinated by the origin of colour in organic molecules. In addition, an understanding of colour and constitution relationships has always been of critical importance in the design of new dyes. In the very early days of synthetic colour chemistry, little was known about the structures of organic molecules. However, following Kekule´’s proposal concerning the structure of benzene in 1865, organic chemistry made significant and rapid progress as a science and, almost immediately, theories concerning the influence of organic structures on the colour of molecules began to appear in the literature. One of the earliest observations of relevance was due to Graebe and Liebermann who, in 1867, noted that treatment of the dyes known at the time with reducing agents caused a rapid destruction of their colour. They concluded, with some justification, that the dyes were unsaturated compounds and that this unsaturation was destroyed by reduction.

Perhaps the most notable early contribution to the science of colour and constitution was due to Witt who, in 1876, proposed that dyes contain two types of groups which are responsible for their colour. The first of these is referred to as the *chromophore*, which is defined as a group of atoms principally responsible for the colour of the dye. Secondly, there are the *auxochromes*, which he suggested were 'salt-forming' groups of atoms whose role, rather more loosely defined, was to provide an essential 'enhancement' of the colour. This terminology is still used to a certain extent today to provide a simple explanation of colour, although Witt's original suggestion that auxochromes were also essential for dyeing properties was quickly recognized as having less validity. A further notable contribution was made by Hewitt and Mitchell who first proposed in 1907 that conjugation is essential for the colour of a dye molecule. In 1928, this concept was incorporated by Dilthey and Witzinger in their refinement of Witt's theory of chromophores and auxochromes. They recognized that the chromophore is commonly an electron-withdrawing group, that auxochromes are usually electron-releasing groups and that they are linked to one another through a conjugated system. In essence, the concept of the donor—acceptor chromogen was born. Furthermore, it was observed that a bathochromic shift of the colour, *i.e.* a shift of the absorption band to longer wavelength, might be obtained by increasing the electron-withdrawing power of the chromophore, by increasing the electron-releasing power of the auxochromes and by extending the length of the conjugation.

The chromophore and auxochrome theory, which was first proposed more than 100 years ago, still retains some merit today as a simple method for explaining the origin of colour in dye molecules although it lacks rigorous theoretical justification. The most important chromophores, as defined in this way, are the azo (-N=N-), carbonyl (-C= O), methine (-CH=) and nitro (NO_2) groups. Commonly-encountered auxochromes, groups that normally increase the intensity of the colour and shift the absorption to longer wavelengths of light, include hydroxyl (-OH) and amino (NR_2) groups. The numerous examples of chemical structures which follow in later sections of this book will illustrate the many ways in which chromophores, auxochromes and conjugated aromatic systems, together with other structural features designed to confer particular application properties, are incorporated into dye and pigment molecules. The concept may be appliedto most chemical classes of dye, including azo, carbonyl, methine and nitro dyes, but for some classes which are not of the donor—acceptor type, for example the phthalocyanines, it is less appropriate. Nowadays, modern theories of chemical bonding, based on either the valence-bond or the molecular orbital approaches, are capable of providing a much more sophisticated account of colour and constitution relationships.

The **valence-bond** approach to colour and constitution requires that certain assumptions be made concerning the structures of the electronic ground state and of the electronic first excited state of the dye molecules. Invariably, a dye molecule may be represented as a resonance hybrid of a large number of resonance forms, some of which are 'neutral' or normal Kekule´-type structures, and some of which involve charge-separation, particularly involving electron release from the donor through to the acceptor groups. For the purpose of explaining the colour of dyes, a first assumption is made that the ground electronic state of the dye most closely resembles the most stable resonance forms, the normal Kekule´-type structures. A second assumption is that the first excited state of the dye more closely resembles the less stable, charge-separated forms. The nature of these assumptions will be clarified by a consideration of the examples that follow. As a consequence of Planck's relationship ($\Delta E = hc/\lambda$), the wavelength at which the dye absorbs increases (a bathochromic shift) as the difference in energy between the ground state and the first excited state decreases. Essentially the valence-bond approach is used to account for these energy differences. Structural factors, both electronic and steric, which either stabilize or destabilize the first excited state relative to the ground state, are analyzed to provide a qualitative explanation of colour. The assumptions which the approach makes concerning the structures of the ground and the first excited states are clearly approximations and cannot be rigorously justified.

In **molecular orbital theory**, electrons are considered as a form of electromagnetic radiation, *i.e*. in terms of their wave nature rather than their particulate nature. A principle of fundamental importance to the theory is the quantum principle, which states that the electron can only exist in a fixed series of discrete energy states. An essential concept in quantum theory of relevance to colour chemistry is that electrons are contained in regions of high probability referred to as *orbitals*. The mathematics underlying molecular orbital theory was first formulated in 1925 by Schrodinger, the solution of whose equation gives a fixed number of values of ΔE which are the energy states available to the electrons in a particular atom or molecule. Unfortunately because of the complexity of the mathematics, even with the computing power currently available, the equation may be solved exactly only for relatively simple atomic and molecular systems. However, a range of approximations may be made to obtain solutions to the equation. Coloured molecules have large molecular frameworks so that approximate methods for solution of the equation to give the required values of ΔE (the energies of molecular orbitals) become even more essential. The simplest of these rely on a range of empirically or semi-empirically derived parameters Molecular orbitals are considered to be generated by overlap of atomic orbitals. There are two types of overlap. Direct or 'end-on' overlap gives rise to δ-orbitals, either bonding types, the low energy orbitals which in the ground state of a molecule are occupied by two electrons, or the high energy anti-bonding (δ*) orbitals which remain unoccupied, while molecular orbitals are obtained by indirect or 'sideways' overlap, for example from overlap of two singly occupied $2p_z$ atomic orbitals.

Dyes are usually organic molecules with extended conjugation, containing a framework of δ-bonds and an associated π-system. The lowest energy electronic transitions occur when an electron is promoted from an occupied π-orbital to an unoccupied π* orbital. It is these π—π* transitions (rather than δ—δ* which are of much higher energy) that give rise to the absorption of organic dyes and pigments in the UV and visible regions of the spectrum.

11.3. METHODS OF DYEING

There are a number of methods of applying dye to a fabric. Although the most common method used for applying natural dyes is the vat method, there are techniques which have been developed to allow patterns to be incorporated during the dying process. It is worth bearing in mind that using natural dyes is a complex art and the skills required for using natural dyes are learned over many years.

Vat Dyeing

In the simplest form of dyeing a textile material is immersed in dye and gradually brought to the boil. Alternatively the fiber is allowed to sit and soak for several hours or days. During this period, agitation is necessary to allow full penetration of the textile by the dyestuff. Depending on the type of fabric and dyestuff used, certain salts or acids may be added to assist absorption of the dye.

The principal difficulty in dyeing mixed yarns and fabrics is to achieve the same colour in both fibers. Cotton fibers may, for instance, absorb dyes rapidly, while the wool fibers will have to be boiled over an extended period to reach the same depth of shade. This could lead to significant damage to the material. In this case a chemical compound would need to be used to restrain the rate at which the cotton fiber takes up the dyestuff. The amount of dyestuff which is used is usually given in the recipe. It is usually quoted as a percentage weight of the fabric to be dyed.

Batik

Batik is a starch resist-dyeing process, developed on the Island of Java in modern-day Indonesia. Colour is prevented from reaching certain areas of a fabric by covering these areas with molten wax. The fabric is starched prior to the design being drawn upon it. The wax is applied with a type of cup with a fine pouring spout, usually made of copper. The technique has been developed to a high art form in Indonesia from where it is exported to many parts of the world. Batik paintings, as well as sarongs and lengths of fabric, are produced. When the fabric is dyed, all waxed areas resist the dyestuff. The wax is then removed by placing the fabric in boiling water. For patterns with many colours the same procedure is repeated until the full design is completed.

Tie-dyeing

Tie-dyeing is another popular artisanal dyeing technique. In this resist-dyeing process, waxed thread is tightly tied around the areas chosen to resist the coloured dyestuff, and the fabric is dipped into the dye.

The waxed thread is then removed and the fabric dried. This process can be repeated for each colour to be added.

11.4. CLASSES OF DYES

Dyes can be classified according to chemical structure or according to their usage or application. Dye chemists usually classify dyes according to chemical structure (i.e., azo dyes, anthraquinone dyes, and phthalocyanine dyes), while dye users or technologists usually classify dyes according to their usage or application (e.g., reactive dyes for cotton and disperse dyes for polyester). Often times, both classifications are used (e.g., a phthalocyanine reactive dye for cotton and an azo disperse dye for polyester).

There are many kinds of dyes, including **acid dyes, basic dyes, direct dyes, disperse dyes, reactive dyes, solvent dyes, sulfur dyes, and vat dyes,** which are characterized by their distinct chemical and physical properties.

Acid dyes are water-soluble anionic dyes, usually containing sulfonic acid groups or carboxylic acid groups, that have a high affinity for wool, other protein fibers (silk), and polyamides (modified acrylics). The lower the pH of the solution, the more rapid the dyeing process is. Chemically, the acid dyes consist of azo (including preformed metal complexes), anthraquinone, and triarylmethane compounds with a few azine, xanthene, ketone imine, nitro, nitroso, and quinophthalone compounds.

Basic dyes, sometimes referred to as **cationic dyes**, are usually the salts of organic bases where the cation form of the molecule has the color. Basic dyes are water soluble and yield colored cations in solution. The principal chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine, and acridine.

Direct dyes are water-soluble anionic dyes, containing sulfonic acid groups, which have a high affinity for cellulosic fibers. Most of the dyes in this class are azo compounds with some stilbenes, phthalocyanines, and oxazines.

Disperse dyes are substantially water-insoluble nonionic dyes. They are the most important class of dyes for dyeing hydrophobic synthetic fibers such as polyester and acetates.

Reactive dyes form a covalent bond with the fiber. A marked advantage of reactive dyes over direct dyes is that their chemical structures are much simpler, their absorption spectra show narrower absorption bands, and the dyeings are much brighter. The principle classes of reactive dyes are azo, triphendioxazine, phthalocyanine, formazan, and anthraquinone.

Solvent dyes are water-insoluble dyes devoid of polar solubilizing groups such as sulfonic acid, carboxylic acid, or quaternary ammonium. They are used to color plastics, gasoline, oils, and waxes.

Solvent dyes are predominantly azo and anthraquinone; however, some phthalocyanines and triarylmethane dyes also are used.

Sulfur dyes are complex molecules containing sulfur obtained from the reaction between selected organic intermediates such as 4-aminophenol or *p*-phenylenediamine and molten sulfur or polysulfide. The actual structures of sulfur dyes are unknown, but it is assumed that they possess sulfur-containing heterocyclic rings. Although they are a small group of dyes, the low cost and good wash fastness properties of the dyeings make this class important from an economic standpoint. Vat dyes are water insoluble. They are formed by the conversion of an insoluble, complex, polycyclic molecule, based on the quinone structure, into a soluble leuco (white/clear) form by treatment with alkalinereducing agents. The leuco form is absorbed onto the medium (usually cellulose) and then reconverted *in situ* to the colored insoluble pigment form, which is trapped within the fiber. The principal classes of vat dyes are anthraquinone and indigoid. This class of dyes is no longer commercially important.

CHECK LIST

Be sure that you understand the concepts listed below. When you are sure make a tick (√) at the front.
I understand …

- the advantages and disadvantages of natural and synthetic dyes
- the theories on chemical constitution of dyes
- the methods of dyeing
- the different classes of dyes
- what chromophores and auxochromes are
- what mordants are

EXERCISES 11.1

1. A chromophore is

a) A group of atoms in a coloured compound

b) A coloured compound

c) A group of atoms in compound responsible for absorption of electromagnetic radiation

d) A group of atoms in a compound responsible for electromagnetic radiation

2. Match the followings

A	**B**
1. Orange I	**i) mordant dye**
2. Aniline yellow	**ii) acid dye**
3. Martius	**iii) fiber reactive dye**
4. Alizarin	**iv) basic dye**

i) direct dye

12. THE LEATHER INDUSTRY

UNIT OBJECTIVES

This unit will enable the student to:

- define tanning
- know the importance leather tanning
- outline the steps in leather manufacturing
- learn the natural and chemical tanning materials
- explain the processes of leather tanning
- list the characteristics of tanned leather

12.1. INTRODUCTION

Activity 12.1 What is leather tanning? Why is leather tanned?

When an animal is alive, its skin is soft, flexible, very tough and hard wearing; it has the ability to allow water vapor to pass out, but it will not allow water in. When the skin dies it loses these characteristics: if it is kept wet it rots, and if it is dried it goes hard and brittle. The process of tanning is to retain the skin's natural properties, to stabilize its structure and at the same time to chemically process it so it will no longer be subject to putrefaction. Thus leather is animal skin that has been treated such that its natural properties are retained. Skin is made up of many bundles of interwoven protein fibers which are able to move in relation to one another when the skin is alive. When the skin dies, these fibers tend to shrivel and stick together. Essentially, the purpose of tanning is to permanently fix the fibers apart by chemical treatment, and to lubricate them so they can move in relation to one another.

Well tanned leather, therefore, retains the properties of flexibility, toughness and wear. It also continues to 'breathe', allowing water vapor to pass through but remaining reasonably water-proof. It is this characteristic which accounts for the comfort of genuine leather shoes and clothing. In addition, the process of tanning imparts the advantage of resistance to heat. This is an important factor in many of the uses of leather. In conjunction with chemical processing, the tanner imparts color, texture and finish to the leather, to enhance its appearance and suit it to today's fashion requirements. Animal skins are converted to leather in an eight step process as follows:

1. Dehairing: The animal skins are steeped in an alkali solution that breaks down the structure of the hair at its weakest point (the root) and so removes the hair.

2. Liming: The hairless skin is immersed in a solution of alkali and sulphide to complete the removal of the hair and to alter the properties of the skin protein (collagen). The collagen becomes chemically modified and swells, leaving a more open structure.
3. Deliming and Bateing: The skin structure is then opened further by treatment with enzymes, and further unwanted material is removed.
4. Pickling: The skins are then treated with acid to preserve them for up to two years.
5. Tanning: This is the most chemically complex step. During tanning, the skin structure is stabilized in its open form by replacing some of the collagen with complex ions of chromium. Depending on the compounds used the color and texture of the leather changes. When leather has been tanned it is able to 'breathe' and to withstand 100oC boiling water, as well as being much more flexible than an untreated dead skin.
6. Neutralizing, Dyeing and Fat Liquoring: The leather is then treated with alkali to neutralize it and so prevent deterioration, and then dyed. This involves fixing a variety of compounds onto the chromium, as that is the most reactive site present. Once the leather is dyed, it is treated with reactive oils that attach themselves to the fibrous structure, improving suppleness and flexibility.
7. Drying: Water is removed from the leather, and its chemical properties stabilized.
8. Finishing: A surface coating is applied to ensure an even color and texture, and to improve its ability to wear. Suede leather is also buffed at this point to give it its distinctive finish.

12.2. RAW MATERIALS

The basic raw material for the most tanning industry is a by-product of the meat processing industry. Cattle hides give leather for shoes (soles and uppers), clothing, belts and upholstery. Calf skins are used for fashionable shoe uppers, gloves and for clothing leathers. Sheep skins and lamb skins with wool on are used for car seats, floor rugs, clothing, bedding and footwear, while, with the wool removed, they are used to produce suede and grain clothing leathers as well as chamois leathers.

12.3. THE TREATMENT PROCESS - PREPARATION FOR TANNING

Activity 12.2 Outline the steps in leather manufacturing. What is genuine leather? What is fake leather? What are its raw materials?

Tanning is the process of treating skins of animals to produce leather, which is more durable and less susceptible to decomposition. Traditionally, tanning used tannin, an acidic chemical compound from which the tanning process draws its name (tannin is in turn named for an old German word for oak or fir trees, which supplied it). Coloring may occur during tanning. A **tannery** is the term for a place where the skins are processed.

Tanning leather involves a process which permanently alters the protein structure of skin. Making "rawhide" (untanned but worked hide) does not require the use of tannin. Rawhide is made by removing the flesh and fat and then the hair by use of an aqueous solution (this process is often called "liming" when using lime and water or "bucking" when using wood ash (lye) and water), then scraping over a beam with a somewhat dull knife, then drying. The two aforementioned solutions for removing the hair also act to clean the fiber network of the skin and allow penetration and action of the tanning agent, so that all the steps in preparation of rawhide except drying are often preludes to the more complex process of tanning and production of leather.

Tanning can be performed with either vegetable or mineral methods. Before tanning, the skins are unhaired, degreased, desalted and soaked in water over a period of 6 hours to 2 days. To prevent damage of the skin by bacterial growth during the soaking period, biocides, typically dithiocarbamates are used. Fungicides such as TCMBT, 2-(Thiocyanomethylthio) benzothiazole, are added later in the process to protect wet leathers from mould growth. After 1980 the use of pentachlorophenol and quicksilver (mercury base) biocides and their derivatives was forbidden.

The main chemical processes carried out by the tanner are the de-hairing, liming, tanning, neutralizing and dyeing**.**

Step 1: Unhairing

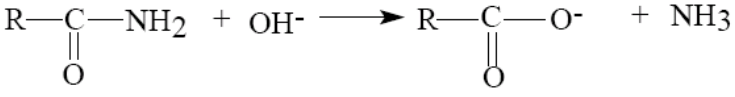
The keratin of hair and wool is subject to attack by alkali, which will break (by hydrolysis) the sulphur-sulphur bond in the cystine linkage of the keratin. The hair is attacked first at the root, where it is in its immature form. After a certain time of being steeped in a solution of alkali (sodium or calcium hydroxide) and a reducing agent, normally sodium sulphide, the hair roots are dissolved, and the hair may be removed and saved. In the processing of sheep and lambskins, the solution of alkali and sulphide is applied on the inside of the skin, allowing the solution to penetrate through the skins, attacking the wool roots, which can then be removed by 'pulling' them from the skin. This is the origin of 'slipe wool', which forms a sizeable portion of New Zealand's wool production.

Step 2: **Liming**

The process of liming is a combination of chemical and physical action on the skin structure. The chemicals involved are similar to those in the unhairing operation. A solution of lime and sodium sulphide is used and the skins are immersed in this solution for whatever time is necessary to produce the desired effects. The process of unhairing is taken to completion during the liming process, and there is appreciable modification of the collagen due to the action of alkali.

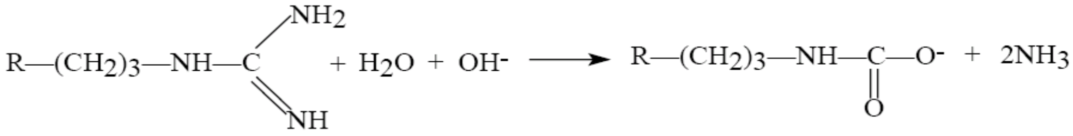
Skin protein (collagen) $\xrightarrow[\text{alkali}]{}$
1) Hydrolysis of amide groups
2) Modification of guanide groups
3) Hydrolysis of keto-imide links in protein chains
4) Swelling
5) Removal of unwanted material

1) Hydrolysis of amide groups



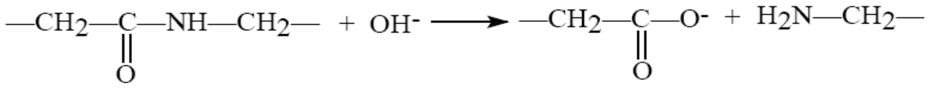
$$R-\underset{\underset{O}{\|}}{C}-NH_2 + OH^- \longrightarrow R-\underset{\underset{O}{\|}}{C}-O^- + NH_3$$

2) Modification of guanide groups (arginine residue)



$$R-(CH_2)_3-NH-C\begin{matrix}\diagup NH_2\\ \diagdown\!\!\diagdown NH\end{matrix} + H_2O + OH^- \longrightarrow R-(CH_2)_3-NH-\underset{\underset{O}{\|}}{C}-O^- + 2NH_3$$

3) hydrolysis of amide linkages in the backbone of the collagen chains



$$-CH_2-\underset{\underset{O}{\|}}{C}-NH-CH_2- + OH^- \longrightarrow -CH_2-\underset{\underset{O}{\|}}{C}-O^- + H_2N-CH_2-$$

4) Swelling

In addition to the chemical action, in the presence of an alkali, swelling of the fibrous structure takes place. This is due to an osmotic pressure effect. The result is the separation of the fibres and the fibrils from one another and an opening up of the whole structure.

5) Removal of unwanted material

Present in the collagen structure are globular proteins and other interfibrillary substances. These are hydrolyzed and removed in the subsequent washing and bateing processes. Unwanted fats are saponified.

Step 3: De-liming and Bateing

After the strong alkaline action, the skin structure is further opened up during the deliming and bateing process. Bateing is an enzyme digestion process which continues the cleaning up process begun by the alkaline action. Bateing is carried out at pH 9-10. This is achieved by treatment with acid salts (ammonium chloride or ammonium sulphate) or carbon dioxide until the desired pH is reached.

Hydrolysis is continued by the enzyme process and further dissolution of unwanted material occurs. The main fibrous network is then cleaned up and the swelling is reduced.

Step 4: Pickling

The main acidification process is that of pickling. The skins are agitated in a solution of salt and sulphuric acid until they are at or near equilibrium at a pH value of 3.0 - 3.5.

12.4. VEGETABLE TANNING

Vegetable tanning uses tannin (this is the origin of the name of the process). The tannins (a class of polyphenol, a stringent chemical) occur naturally in the bark and leaves of many plants. Tannins bind to the collagen proteins in the hide and coat them causing them to become less water-soluble, and more resistant to bacterial attack. The process also causes the hide to become more flexible. The primary barks, processed in Bark mills and used in modern times are chestnut, oak, redoul, tanoak, hemlock, quebracho, mangrove, wattle (acacia), and myrobalan. Hides are stretched on frames and immersed for several weeks in vats of increasing concentrations of tannin. Vegetable tanned hide is flexible and is used for luggage and furniture.

12.5. MINERAL TANNING

Prior to the introduction of the basic chromium species in tanning, several steps are required to produce a tannable hide. These steps include scudding or removing the hair, liming or the introduction of alkali agents such as sodium hydroxide, de-liming or restoring neutral pH, bating or softening the skin with enzymes, and pickling or lowering pH of the hide with salt and sulfuric acid. The pH is very acidic when the chromium is introduced to ensure that the chromium complexes are small enough to fit in between the fibers and residues of the collagen. Once the desired level of penetration of chrome into the substance is achieved, the pH of the material is raised again to facilitate the process. This step is known as "basification". In the raw state chrome tanned skins are blue and therefore referred to as "wet blue." Chrome tanning is faster than vegetable tanning (less than a day for this part of the process) and produces a stretchable leather which is excellent for use in handbags and garments.

12.5.1. CHROME TANNING

Chromium (III) sulfate ($[Cr(H_2O)_6]_2(SO_4)_3$) has long been regarded as the most efficient and effective tanning agent. Chromium (III) compounds of the sort used in tanning are significantly less toxic than hexavalent chromium. Chromium(III) sulfate dissolves to give the hexaaquachromium(III) cation, $[Cr(H_2O)_6]^{3+}$, which at higher pH undergoes processes called olation to give polychromium(III) compounds that are active in tanning, being the cross-linking of the collagen subunits. The chemistry of $[Cr(H_2O)_6]^{3+}$ is more complex in the tanning bath rather than in water due to the presence of a variety of ligands. Some ligands include the sulfate anion, the collagen's carboxyl groups, amine groups from the side chains of the amino acids, as well as "masking agents." Masking agents are carboxylic acids, such as acetic acid, used to suppress formation of polychromium (III) chains. Masking agents allow the tanner to further increase the pH to increase collagen's reactivity without inhibiting the penetration of the chromium (III) complexes.

Collagen is characterized by a high content of glycine, proline, and hydroxyproline, usually in the repeat -gly-pro-hypro-gly-. These residues give rise to collagen's helical structure. Collagen's high content of hydroxyproline allows for significant cross-linking by hydrogen bonding within the helical structure. Ionized carboxyl groups (RCO_2^-) are formed by hydrolysis of the collagen by the action of hydroxide. This conversion occurs during the liming process, before introduction of the tanning agent (chromium salts). The ionized carboxyl groups coordinate as ligands to the chromium (III) centers of the oxo-hydroxide clusters. Tanning increases the spacing between protein chains in collagen from 10 to 17 Å. The difference is consistent with cross-linking by polychromium species, of the sort arising from olation and oxolation.

Possible Chromium (III) Tanning Mechanisms

Subsequent to application of the chromium agent, the bath is treated with sodium bicarbonate to increase the pH to 4.0-4.3. This increase induces cross-linking between the chromium and the collagen. The pH increase is normally accompanied by a gradual temperature increase up to 40 °C. Chromium's ability to form such stable bridged bonds explains why it is considered one of the most efficient tanning compounds. Chromium-tanned leather can contain between 4 and 5% of chromium. This efficiency is characterized by its increased hydrothermal stability of the skin, and its resistance to shrinkage in heated water.

12.5.2. TAWING: ALUM TANNING

Tawing is a method that uses alum and aluminium salts, generally in conjunction with other products such as egg yolk, flour, and other salts. The leather becomes tawed by soaking in warm potash alum and salts solution between 20°C and 30°C. The process increases the leather's pliability, stretchability, softness, and quality. Adding egg yolk and flour to the standard soaking solution further enhances its fine handling characteristics. Then, the leather is air dried ("crusted") for several weeks, which allows it to stabilize.

Tawing is traditionally used on pigskins and goatskins to create the whitest colors. However, exposure and aging may cause slight yellowing over time and, if it remains in a wet condition, tawed leather will suffer from decay. Technically, tawing is not tanning.

12.6. LEATHER FINISHING

The final stage, known as finishing, is used to apply finishing material to the surface or finish the surface without the application of any chemicals if so desired. Depending on the finish desired, the hide may be waxed, rolled, lubricated, injected with oil, split, shaved and, of course, dyed.

EXERCISES 12.1

1. **Which of the following is a pre-tanning process?**

   a) **De-hairing** **b) liming** **c) neutralizing** **d) finishing**

2. **Matching**

A	**B**
1. Baiting	a) treatment with alkali
2. Scudding	b) restoring neutral PH
3. Liming	c) lowering PH of hide with salt and H_2SO_4
4. De-liming	d) softening the skin with enzymes
5. Pickling	e) removing the hai

ANSWER KEYS FOR SELCTED SELF-TEST EXERCISE

Exercise 6.1

1. Paints, Cosmetics, Polymers, Energy, Lubricants, and Surfactants
2. Anionic, cationic, amphoteric or nonionic
3. (a) Cloud point (b) Kraft point (c) Surface tension and interfacial tension
   (d) Critical micelle concentration

Exercise 8.1

1. Ethanol(Beverages), Antibiotics(eg.penicillin), Chemicals(Citric, acetic acid etc), Dairy product(Cheese, yogurt)
2. Wort is sugar solution that is extracted from the grains. . The "spent grains" are removed and sold as cattle feed. The liquid obtained by sparking is the wort which undergoes several processes to make a beer. Beer is the end product.

3. To convert the unfermentable starches of the barley into fermentable simple sugars.
4. Distillation is possible when there is a difference in the boiling point of liquid mixture.
5. To remove insoluble solids and microorganisms
6. To inhibits the growth of wild microorganisms and prevents oxidative browning of the juice.

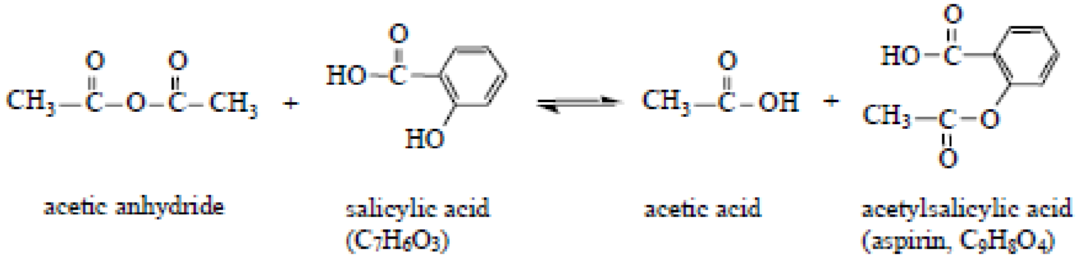
Exercise 9.1

1. Bactericidal = kill bacterial cells, bacteriostatic = inhibit cell growth

2. Anti malarial agents act as: Gametocytocides, Sporozoitocide, Schizonticides

Anti bacterial agents act as: i) Inhibition of bacterial cell wall synthesis
ii) Interactions with the plasma membrane.
iii) Disruption of protein synthesis
iv) Inhibition of nucleic acid transcription and replication.

3.



Exercise 10.1

1) a 2) b 3) b 4) b 5) d

Exercise 11.1

1) c
2) 1) ii 2) iv 3) v 4) i

Exercise 12.1

1) a
2) 1) d 2) e 3) a 4) b 5) c