
UNIT 3 LIPIDS

Structure

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3.1 INTRODUCTION

After a detailed study on carbohydrates, we now move on to the next structural component of all living cells, the lipids. Lipids are the major components of adipose tissue and together with the proteins and carbohydrates they constitute the principal structural components of all living cells.

Lipids in food exhibit unique physical and chemical properties. Their composition, crystalline structure, melting properties and the ability to associate with water and other non-lipid molecules are especially important to their functional properties in many foods. We will learn about these properties and the role of lipids in product preparation in this unit. Further, during the processing, storage and handling of foods, lipids undergo complex chemical changes and react with other food constituents, producing numerous compounds, both desirable and deleterious to the food quality. What are these

deteriorative changes in food lipids? Are there any means of controlling such changes? These are the other issues highlighted in this unit.

You will realize, that like in previous two units, here too we have not dwelt much on the structural component of lipids. The reason being that the structure, physical/chemical properties have been discussed in the Nutritional biochemistry course. We do not wish to duplicate the effort here and make the content bulky. However, we do advise you to look up the relevant block/unit in the Nutritional Biochemistry course before you start studying this unit. Best approach would be to have those blocks handy so that you can refer to them as and when required.

Objectives

After studying this unit, you will be able to:

- enumerate the important sources of food lipids,
- describe the basic composition of food lipids,
- discuss the role of food lipids in product preparation,
- debate on the importance of functionality of food lipids with reference to food processing and quality of finished products, and
- recognize the deteriorative changes in food lipids and means of controlling such changes.

3.2 LIPIDS – INTRODUCTION AND SOURCES

In its broadest sense, ‘lipids’ defines substances as oils, fats and waxes which can be only characterized by a large array of properties. They are in general:

- coming from plant and animal origin;
- insoluble or immiscible with water but soluble in organic solvents such as chloroform, ether, benzene, acetone; and
- formed of long-chain hydrocarbon groups (carbon and hydrogen), but may also contain oxygen, phosphorous, nitrogen and sulphur.

Glycerol esters of fatty acids, which make up to 99% of the lipids of plant and animal origin have been traditionally called *fats and oils*. This distinction, based solely on whether the material is solid or liquid at room temperature, is of little practical importance and the two terms are often used interchangeably.

Food lipids are either consumed in the form of “*visible*” fats, which have been separated from the original plant or animal sources, such as vegetable oil and butter, or as constituents of basic foods, such as milk, cheese and meat. This is referred to as ‘*invisible fat*’. You already know that dietary lipids play an important role in nutrition. They supply calories and essential fatty acids, act as vitamin carriers and increase the palatability of food. The largest supply of vegetable oil comes from the seeds of soy bean, cottonseed, peanut and the oil-bearing trees of palm, coconut and olive.

Oil-bearing fruits, nuts and seeds have been grown and used for food for many centuries. More than 100 varieties of plants are known to have oil-bearing seeds, but only a few have been commercialized. The largest source of vegetable oil at present is the seeds of annual plants such as soybean, cottonseed, peanut, sunflower, safflower, mustard and rapeseed. Many of the oil-bearing seeds are not only a source of oil, but also protein, the protein portion has the most value. A second source of vegetable oils is the oil-bearing fruits and nuts of trees such as coconut, palm, palm kernel and olive. The oil from the palm and olive is extracted from the fruit rather than the seed of the fruit. All the oil-bearing trees require a relatively warm climate, two of which are tropical: coconut and palm.

Oil contents for vegetable oil-bearing materials vary between 18% and 68% of the total weight of the seed, nut, kernel or fruit as indicated in Table 3.1.

Table 3.1: Oil Content of few Vegetable Oil Sources

Oil Bearing Material	Oil Content (%)
Coconut	65 – 68
Cottonseed	18 – 20
Olive	25 – 30
Palm	45 – 50
Palm kernel	45 – 50
Peanut	45 – 50
Safflower	30 – 35
Soybean	18 – 20
Sunflower	35 – 45

Meat fats are derived almost entirely from three kinds of domestic animals: hogs, cattle and sheep. Milk of cow and buffalo is an important source of fat in the form of either butter or ghee. Bulk of the world's milk fat production consists of butterfat from cow's milk, and in India, butter and ghee have a well-established place in the culinary practices.

Fats and oils are a unique class of agricultural products in that a high degree of interchangeability among them is possible for many products and uses. Additional processing and/or blending of one or more source oils may be necessary for a satisfactory substitution. Knowledge of the physical and chemical properties of each individual raw material is necessary to successfully duplicate or improve on the functionality of the original source oil's functionality. To understand this, we need to first look at the composition of lipids. The next section is devoted to the classification and composition of lipids.

3.3 LIPIDS - CLASSIFICATION AND COMPOSITION

The classification and categories of lipids is presented in this section. There may be different ways of classifying lipids. A general classification is presented herewith.

You may recall reading about the classification of lipids in the Advance Nutrition Course.

3.3.1 Classification of lipids

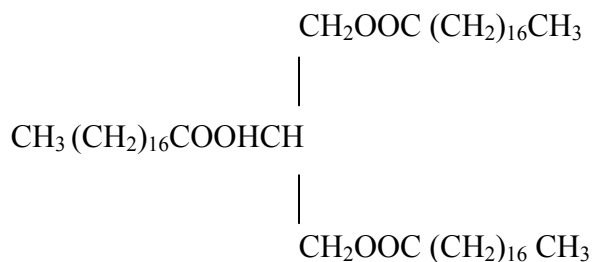
A general classification of lipids based on their structural components is presented in table 3.2. Such a classification, however, is possibly too rigid for a group of compounds as diverse as lipids and should be used only as a guide. The table gives the major, subclass and description of the various lipids.

Table 3.2: Classification of lipids

Major Class	Subclass	Description
Simple lipids	Acylglycerols	Glycerol + fatty acids
	Waxes	Long-chain alcohol + long-chain fatty acids
Compound lipids	Phosphoacylglycerols (or glycerophospholipids)	Glycerol + fatty acids + phosphate + another group usually containing nitrogen
	Sphingomyelins	Sphingosine + fatty acid + phosphate + choline
	Cerebrosides	Sphingosine + fatty acid + simple sugar
	Gangliosides	Sphingosine + fatty acid + Complex carbohydrate moiety that includes sialic acid
Derived lipids	Materials that meet the definition of a lipid but are not simple or compound lipids	Examples: fatty acids, carotenoids, steroids, fat-soluble vitamins

It should also be recognized that other classifications may sometimes be more useful. For example, the sphingomyelins can be classed as phospholipids because of the presence of phosphate. The cerebrosides and the gangliosides can also be classified as glycolipids because of the presence of carbohydrate and the sphingomyelins. The glycolipids can be classed as sphingolipids because of the presence of sphingosine.

The most abundant class of food lipids is the acylglycerols, also known as *glycerol esters of fatty acids*, which dominate the composition of depot fats in animals and plants. The polar lipids are found almost entirely in cellular membranes (phospholipids being the main component of the bilayer), with only very small amounts in depot fats. In some plants, glycolipids constitute the major polar lipids in cell membranes. Waxes are found as protective coatings on skin, leaves and fruits. Major components of lipids are the acylglycerols. They are the esters of glycerol and fatty acids, having a varying chain length. Fatty acids are aliphatic monocarboxylic acids that can be liberated by hydrolysis from naturally-occurring fats. For example, oleic acid, which is a common fatty acid found in acylglycerols, has 18 carbon atoms in its chain. The carboxyl (COOH) group of the acids forms the ester by combining with the hydroxyl (OH) group of glycerol. There are 3 hydroxyl groups in a glycerol molecule. If all the three groups are forming ester linkage with fatty acids, the resulting compound is called a triacylglycerol or a *triglyceride*. Structure of a triacylglycerol is shown:



The compound shown here is tristearoylglycerol, also known as glycerol tristearate. This is a triester of glycerol with stearic acid. Many other fatty acids either saturated or unsaturated and having varying chain length are present in triacylglycerols.

Common fatty acids present in acylglycerols are stearic acid (C-18, saturated), oleic acid (C-18, monounsaturated), linoleic acid (C-18, diunsaturated) and palmitic acid (C-16, saturated).

You came across the terms saturated and unsaturated in the above section. Let's understand these terms better.

3.3.2 Categories of Fats and Oils

As a student of nutrition, you already know that fatty acids are the lipid-building blocks. It is customary to divide the fatty acids into different groups, e.g., saturated and unsaturated ones. *Saturated* meaning they have as many hydrogens bonded to their carbons as possible and *unsaturated* meaning with one or more double bonds connecting their carbons, hence, fewer hydrogens. This particular division is useful in food technology because saturated fatty acids have a much higher melting point than the unsaturated ones, and the ratio of these fatty acids is of major importance for the physical properties of a fat or oil.

Table 3.3a. Saturated fatty acids

Systematic Name	Common Name	Formula	Short-hand Description
n-Butanoic	Butyric	$\text{CH}_3 (\text{CH}_2)_2 \text{COOH}$	4:0
n-Hexanoic	Caproic	$\text{CH}_3 (\text{CH}_2)_4 \text{COOH}$	6:0
n-Octanoic	Caprylic	$\text{CH}_3 (\text{CH}_2)_6 \text{COOH}$	8:0
n-Decanoic	Capric	$\text{CH}_3 (\text{CH}_2)_8 \text{COOH}$	10:0
n-Dodecanoic	Lauric	$\text{CH}_3 (\text{CH}_2)_{10} \text{COOH}$	12:0
n-Tetradecanoic	Myristic	$\text{CH}_3 (\text{CH}_2)_{12} \text{COOH}$	14:0
n-Hexadecanoic	Palmitic	$\text{CH}_3 (\text{CH}_2)_{14} \text{COOH}$	16:0
n-Octadecanoic	Stearic	$\text{CH}_3 (\text{CH}_2)_{16} \text{COOH}$	18:0

n-Eicosanoic	Arachidic	$\text{CH}_3 (\text{CH}_2)_{18} \text{COOH}$	20:0
n-Docosanoic	Behenic	$\text{CH}_3 (\text{CH}_2)_{20} \text{COOH}$	22:0

Some of the more important saturated fatty acids with their systematic and common names are listed in table 3.3a, and some of the unsaturated fatty acids in table 3.3b. The naturally occurring unsaturated fatty acids in fats are almost exclusively in the *cis* – form, although *trans* – acids are abundant in ruminant milk fats and in catalytically hydrogenated fats. What are *cis* and *trans*-acids? You may have learnt about this concept in the Nutritional Biochemistry Course. We suggest you look up Block 1, Unit 2 of the Nutritional Biochemistry course for understanding this concept.

Table 3.3 b. Unsaturated Fatty Acids

Systematic Name	Common Name	Formula	Short-hand Description
Hexadec-9-enoic	Palmitoleic	$\text{CH}_3 (\text{CH}_2)_5 \text{CH}=\text{CH} (\text{CH}_2)_7 \text{COOH}$	16:1
Octadec-9-enoic	Oleic	$\text{CH}_3 (\text{CH}_2)_7 \text{CH}=\text{CH} (\text{CH}_2)_7 \text{COOH}$	18:1
Octadeca-9:12-dienoic	Linoleic	$\text{CH}_3 (\text{CH}_2)_4 (\text{CH}=\text{CH}.\text{CH}_2)_2 (\text{CH}_2)_6 \text{COOH}$	18:2
Octadeca-9:12:15-trienoic	Linolenic	$\text{CH}_3 (\text{CH}_2)_3 (\text{CH}=\text{CH}.\text{CH}_2)_3 (\text{CH}_2)_6 \text{COOH}$	18:3
Eicosa-5:8:11:14-tetraenoic	Arachidonic	$\text{CH}_3 (\text{CH}_2)_4 (\text{CH}=\text{CH}.\text{CH}_2)_4 (\text{CH}_2)_2 \text{COOH}$	20:4
Docos-13-enoic	Erucic	$\text{CH}_3 (\text{CH}_2)_7 \text{CH}=\text{CH} (\text{CH}_2)_{11} \text{COOH}$	22:1

Table 3.4 gives the composition of common vegetable oils.

Table 3.4: Component Fatty acids of some vegetable oils (Wt %)

Oil	Fatty Acids								
	16:0	18:0	20:0	22:0	24:0	16:1	18:1	18:2	18:3
Cottonseed	22	3	Tr	---	---	1	19	54	1
Peanut	11	2	2	3	1	Tr	48	32	---
Sunflower	7	5	---	---	---	---	19	68	---
Corn	11	2	Tr	Tr	---	---	28	58	---

Sesame	9	4	---	---	---	---	41	45	---
Olive	13	3	Tr	---	---	2	71	10	1
Palm	45	4	---	---	---	---	40	10	---
Soybean	11	4	Tr	Tr	---	---	24	54	7
Safflower	7	2	Tr	---	---	---	13	78	---
*Mustard	3.5	---	---	---	---	---	22.4	24.4	13.7

* also contains around 40% Erucic acid (22:1)

Tr- Traces

In continuation of our classification of lipids, it is important to realize that edible fats are traditionally classified into the following subgroups:

Milk Fats

Fats of this group are derived from the milk of ruminants, particularly cows and buffaloes. Although the major fatty acids of milk fat are palmitic, oleic and stearic, this fat is unique among animal fats in that it contains appreciable amounts of the shorter chain fatty acids (C4 to C12), small amounts of branched and odd numbered acids and fatty acids with trans-double bonds.

Lauric Fats

Fats of this group are derived from certain species of palm, such as coconut. The fats are characterized by their high content of lauric acid (40 – 50%), moderate amounts of C6, C8 and C10 fatty acids, low content of unsaturated acids and low melting points.

Vegetable Butters

Fats of this group are derived from the seeds of various tropical trees and are distinguished by their narrow melting range, which is due mainly to the arrangement of fatty acids in the triacylglycerol molecules. In spite of their large ratio of saturated to unsaturated fatty acids, trisaturated acylglycerol are not present. The vegetable butters are extensively used in the manufacture of confections, with cocoa butter being the most important member of the group.

Oleic – Linoleic Fats

Fats in this group are the most abundant. The oils are all of vegetable origin and contain large amounts of oleic and linoleic acids, and less than 20% saturated fatty acids. The most important members of this group are cottonseed, corn, peanut, sunflower, safflower, olive, palm and sesame oils.

Linolenic Acids

Fats in this group contain substantial amounts of linolenic acid (C₁₈ triunsaturated). Examples are soybean, mustard, rapeseed, flaxseed and wheat germ hempseed and perilla oils, with soybean being the most important. The abundance of linolenic acid in soybean oil is responsible for the development of an off-flavour problem known as ‘flavour reversion’.

Animal Fats

This group consists of depot fats from domestic land animals (e.g., lard and tallow), all containing large amounts of C₁₆ and C₁₈ fatty acids, medium amounts of unsaturated acids, mostly oleic and linoleic and small amounts of odd numbered acids. These fats also contain appreciable amounts of fully saturated triacylglycerols and exhibit relatively high melting points. Egg lipids are of particular importance because of their emulsifying properties and their high content of cholesterol.

The lipid content of whole eggs is approximately 12%, almost exclusively present in the yolk, which contains 32 – 36% lipid. The major fatty acids in egg yolks are 18: 1 (38%), 16: 0 (23%), and 18: 2 (16%). Yolk lipids consist of about 66% triacylglycerols, 28% phospholipids and 5% cholesterol. The major phospholipids of egg yolk are phosphatidylcholine (73%) and phosphatidylethanolamine (15%).

Marine oils

These oils typically contain large amounts of long – chain omega-3-polyunsaturated fatty acids, with up to six double bonds and they are usually rich in vitamins A and D. Because

of their high degree of unsaturation, they are less resistant to oxidation than other animal or vegetable oils.

With this, we come to the end of first part of this unit i.e., the introduction, classification and composition of lipids. Look up the points to remember given herewith. They are the useful hints/tips for remembering the concept on your finger tips. Read them carefully.

Points to Remember

1. Lipids consist of group of compounds that are generally soluble in organic solvents but only sparingly soluble in water.
2. Glycerol esters of fatty acids (Acylglycerols) which make up to 99% of the lipids of plant and animal origin have been traditionally called fats and oils.
3. Common fatty acid present in acyl glycerols are stearic acid (C-18, saturated), oleic acid (C-18, monounsaturated), linoleic (C-18, di unsaturated) and palmitic (C-16, saturated).
4. Major sources of oils and fats are peanut (groundnut), mustard, soybean, sunflower, coconut, palm and milk.
5. Fats and oils belonging to oleic-linoleic acid group are the most abundant. They contain large amounts of oleic acid (C-18 mono unsaturated) and linoleic acid (C-18 diunsaturated) and less than 20% saturated fatty acids.
6. Important members of oleic-linoleic acid group are peanut, sunflower, cotton seed and sesame oils.
7. Milk fat is unique because it contains appreciable amounts of shorter chain acids (C-4 to C-12).
8. Animal fats contain appreciable amounts of fully saturated triacylglycerols and exhibit relatively high melting points.

Check your progress Exercise 1

1. Define lipids and mention main sources of lipids.

2. What is role of food lipids in human diet?

3. Mention the major classes of lipids and describe acylglycerols.

4. Name the categories of fats and oils with examples.

5. What are the main differences between vegetable oil and animal fats?

Next, let us look at the functional properties of food lipids.

3.4 FUNCTIONAL PROPERTIES OF FOOD LIPIDS

Chemically, fats and oils, as you may already know by now, are a combination of glycerol and fatty acids. The glycerol molecule has three separate points, where a fatty acid molecule can be attached. Physically, fats and oils differ in that fats are solid and oils are liquid at room temperature. You learnt earlier that the different properties are to a large extent determined by the fatty acid composition and the extent of saturation or unsaturation present. These aspects are identified by the carbon chain length and the number and position of double bonds for the individual fatty acids and their position of the glycerol. Generally, solid fats indicated by a dominance of saturated fatty acids and liquid oils, are an evidence of a high level of unsaturated fatty acids.

Carbon chain lengths of fatty acids in edible oils and fats vary between 4 and 24 carbon atoms with up to three double bonds. The most prevalent saturated fatty acids are lauric (C-12:0), myristic (C-14:0), palmitic (C-16:0), stearic (C-18:0), arachidic (C-20:0), behenic (C-22:0) and lignoceric (C-24:0). The most important monounsaturated fatty acids are oleic (C-18:1) and erucic (C-22:1). The polyunsaturated fatty acids are linoleic (C-18:2) and linolenic (C-18:3).

Natural fats and oils vary widely in their physical properties even though they are composed of the same or similar fatty acids. These differences result from differences in the proportion of the fatty acids and the structure of the individual triglycerides. Factors that affect the properties of vegetable oil are plant maturity, plant health, microbiological, seed location within the flower and the genetic variation of the plant. Animal fats and oils composition varies according to the animal species, diet, health and fat location on the carcass and maturity.

Physical properties of an oil or fat are of critical importance in determining its functional characteristics or use in food products. One fundamental physical property of importance is demonstrated by the terms *fats* and *oils*, which indicate whether a lipid is a solid or liquid at ambient temperatures. But this grouping is not rigid because vegetable oils that are solid at ambient temperatures in a temperate climate are liquid at the tropical ambient temperatures. How then can one measure the functional properties? Have you come across the term performance testing? The next section presents a detailed discussion on this aspect.

3.4.1 Measurement of Functional Property

Fats and oils have several functional properties that affect the quality of processed foods. In deep fat frying, the roles played by the frying oil are many: These include:

1. It acts as an effective heat exchange medium leading to cooking of the product being fried and evaporation of water from the product,
2. It helps in the development of texture of fried food.

3. Oil absorbed by the products provides characteristic fried taste and flavour. In the preparation of the baked products, presence of fat contributes to texture and flavour. Fats and oils form emulsion in batters and doughs leading to the development of desirable structure and texture on baking or toasting.

Some essential attributes contributed by fats and oils cannot be directly measured with chemical or physical analytical methods. In these cases, *performance testing* is the only means for evaluating the ability of fat or oil to perform the desired functions in a food product. Actual determinations of the performance qualities of an edible fat and oil product are made with small scale practical tests that evaluate a finished product. *Performance testing is essential for the development of new products, especially for fats and oils products designed for a specific food product, a formulation, or a process.* After development, physical or chemical analysis can be related to performance results in most situations; however, continuation of certain performance evaluations is necessary for some products to ensure adequate performance or more timely results in some cases. Initially, most performance testing was designed for bakery products but has now been expanded to every specialty product situation, i.e., baking, frying, candy, coatings, formulated foods, nondairy products, and so forth, wherever tailored oils, margarines, oils and other specialty products are utilized. In many cases the performance tests are developed to evaluate the fat and oil ingredient as it would be used by a specific food processor. You would realize, performance evaluation in itself can be a detailed subject of study. Here, in this unit we shall not dwell on this aspect. Those of you, who are interested to learn more about performance evaluation, read box 1 for information. It provides a few examples of performance evaluation.

Box 1: Performance Evaluation, a few examples

Creaming volume – Cake batter aeration can be affected by the plasticity, consistency, emulsification, bake stock formulation and other fats and oil properties. *Creaming volume evaluations measure the ability of an oil or margarine to incorporate and retain air in a cake batter.* In most cases, batter aeration is an indicator of the baked cake volume, grain and texture and materially affects the handling qualities of the cake batter.

The creaming volume test formula consists of only three ingredients: (1) Test oil or margarine, (2) granulated sugar, and (3) whole eggs. This procedure is the first stage of an old fashion pound cake, where all of the cake batter aeration depended upon the creaming properties of the oil with whole eggs. Batter specific gravities are determined after mixing for 15 minutes and again after 20 minutes. Continued aeration, identified by a decrease in batter specific gravity, indicates that the fat or oil product has a stable consistency that has not broken down to allow the release of air from the batter. Specific gravity is expressed as grams per cubic centimeter per 100 grams, calculated by multiplying the reciprocal of the specific gravity by 100. Specific volume better illustrates the amount or degree of aeration. The performance test is applicable to emulsified, as well as non emulsified products, to measure aeration potential in a cake batter.

Pound cake test – In some cases, oil or margarine creaming volume is most accurately measured by preparing a regular pound cake, omitting the chemical leavener and measuring the volume, grain and texture of the baked cake. Creaming volume, as determined by this method, is affected by batter mixing temperature. Working range or creaming range can be measured by adjusting the finished batter temperature over the desired temperature range. The results obtained in this manner provide a good indication of the creaming range or oil temperature tolerance. The baked pound cake volume is determined by a seed displacement procedure and the cake appearance rated numerically with a scale similar to that provided in table 3.5.

Table 3.5: Rating Scale for Cake

Score	Rating	Description
10	Perfect	Fine regular grains; no holes, cracks, or tunnels; Very thin cell walls and perfect symmetry
9	Very Good	Close regular grain; free of holes, cracks or tunnels, may have occasional hole, good cell wall thickness
8	Good	Grain very slightly open but regular, free of cracks or tunnels, may have occasional hole, good cell

		wall thickness
7	Satisfactory	Grain slightly open, mostly regular, a few small holes, no tunnels or racks, slightly thick cell walls
6	Poor	Open or irregular grain, or frequent holes, some cracks or tunnels
5	Unsatisfactory	Very open or irregular grain, or numerous holes, cracks or tunnels, or thick heavy cell walls; may have solid streaks or gum line
4 and below	Bad	Increasing degrees of unsatisfactory performance

Cake mix evaluation – Originally, cake mix formulations were very similar to bakery cakes and utilized standard “Hi-Ratio” cake oils; however, development of improved cake mixes required rapid aerating oils to minimize mixing times for the house wife, while at the same time increasing the product’s mixing and baking tolerances. The competitive nature of the cake mix industry has continued the demands for new and improved products, of which oil has always been a major contributor. A basic white mix cake formulation and the make-up procedure can serve to evaluate new or revised emulsifier systems for aeration, eating qualities and cake shelf-life, as well as the oil carrier for lubrication and consistency.

Restaurant deep fat frying evaluation – A number of factors are studied when evaluating frying oils. During deep fat frying, the fat is exposed continuously to elevated temperatures in the presence of air and moisture. A number of chemical reactions, including oxidation and hydrolysis, occur during this time, as well as changes due to thermal decomposition. As these reactions proceed, the functional, sensory and nutritional quality of the frying fat changes and eventually reaches a point where it is no longer possible to prepare quality fried products and the fat will have to be discarded. The rate of frying fat deterioration varies with the food fried, the frying fat utilized, the fryer design and the operating conditions.

The deep fat frying evaluation consists of controlled heating of the test oils at $360 \pm 10^{\circ}\text{F}$ (176 to 187°C) continuously until the test is terminated. Fresh French cut potatoes (227 grams) fried three times daily for 7 minutes at 3-hour interval are flavoured once daily.

Frying observations recorded after each frying includes smoking, odor, clarity, gum formation and a determination of foam development. Foam development described as none, trace, slight, definite and persistent should also be measured with a foam test daily and each time a change in the observed foam is recorded. Samples are taken after each 24-hour period for analysis of colour, free fatty acid and iodine value for quantitative measurement of darkening, hydrolysis and polymerization. The frying test is terminated when persistent foam has been observed and substantiated by foam height testing.

We have read about the deep fat frying evaluation method for measurement of functional properties of fat. Deep fat frying is commonly used as a cooking method in most homes. What are the issues to be considered while using this method of cooking is the focus of discussion in the next section.

3.5 DEEP FAT FRYING

Deep fat frying, as you may already know, is the method which involves cooking food in hot fat/oil. The fat immediately surrounds the food and cooks it from all sides, creating an exterior layer that seals in the food's flavors and juices inside. Deep frying is one of surest ways of locking in flavor and developing great texture (also known as "crunch") in cooking. Deep fat frying, in fact, has become one of the more important methods of food preparation used by the food service, snack and baking industries, as well as the home kitchen. The deep fat frying process consists most simply of (1) partially or totally immersing the food prepared for frying into (2) a body of heated frying fat, which is (3) contained in a metal vessel, and (4) maintaining the food in the fat at the appropriate frying temperature for (5) the duration required to cook the product. Going into the cooking utensil are (a) frying fat, (b) heat, and (c) the food prepared for frying. Emerging from the utensil are (a) steam and steam- entraining frying fat, (b) volatile by-products of heating and frying, (c) the finished product, and (d) with filtering, the crumbs or foreign solid by-products of the frying operation.

As you read the next section, you will realize all these factors mentioned above, have a role to play in the deep fat frying process. Let us get to know them.

3.5.1 Factors affecting the process of deep fat frying.

The common factors influencing the process of deep frying include:

1. *Heat*- Frying temperatures ranging from 150 –190°C are necessary to properly prepare the different fried food products. Unfortunately, exposure to high temperatures accelerates all of the breakdown reactions of fats and oils.
2. *Air*- Oxygen from the air is necessary to sustain human life, but it also reacts with the double bonds in the frying oils to oxidize the unsaturated fatty acids, which results in offensive odors and flavours and promotes gum formation or polymerization.
3. *Moisture*- All food products contain moisture, which causes hydrolysis of fats and oils, resulting in an increased fat absorption in most foods.
4. *Contamination*- Any material associated with the frying process that causes the frying media to deteriorate or accelerate the process is a contaminant. Some examples of frying fat contaminants are:
 - *Trace metals* – Most metals are pro-oxidants that exert a marked catalytic effect to accelerate fat breakdown, but some metals are much more active than others. These pro-oxidants can be picked up during processing or storage, from frying equipment, the food fried, or some other contact with a metal. Two metals that promote more rapid breakdown of frying than others are brass and copper.
 - *Soap or detergent*- Residue of these materials from cleaning storage tanks, fryers, or utensils which will catalyze fat breakdown.
 - *Gums or polymerized fats*- Addition of polymerized fats or oils to fresh oils act as catalysts to accelerate the formation of more gums, which contribute to foaming and darkening.
 - *Burnt food particles*- Food particles allowed to remain in the frying fat impart a bitter, caramelized and / or burnt taste along with an unappealing appearance to the food fried and accelerate frying oil breakdown.
5. *Time* – The extent of the frying oil's exposure to the effects of the above factors determines the degree of product deterioration.

So now you realize, the simple process of deep frying is not actually so simple. Utmost care needs to be taken while using this method to ensure that the quality of the frying oil is maintained. The next section is devoted to this crucial practical aspect i.e., maintaining the quality of fried oils.

3.5.2 Maintaining the quality of frying oil

As frying continues, the level of oil in the fryer depletes. There are two beneficial frying fat quality factors affected during the frying operation. These include:

- the steam released during frying, and
- the addition of fresh oil to replace the fat absorbed by the food fried.

Steam formed from the moisture released from the food mixes intimately with the fat, and when given off, it carries with it the odor- and flavour-bearing volatile by-products of frying that would otherwise accumulate in the frying fat to adversely affect the flavour and odor of the fried food. This steam continually scrubs or purges the frying fat of the potential off – flavours and odors each time the food is fried, even though it is the same moisture that causes hydrolysis. Fresh oil must be added to the fryer to compensate for the fat removed by the fried product. This addition helps to overcome the changes to the frying fat brought about by the heat and other frying fat enemies. Obviously, the frying fat will remain in better condition when higher replacement oil quantities are required. The ratio of the fryer's capacity to the rate at which the fresh oil is added to replenish the fryer is referred to as *turnover rate, or the number of hours required for the addition of fresh frying oil equal to the amount of fat maintained in the fryer*. Because oxidative changes occur continuously in heated fats, turnover must be related to the total period that the fat is heated, rather than only the actual time the product is fried. Obviously, the quality and, especially, the flavour of the frying fat will be maintained at a more desirable level with the highest turnover rate. In general, an operation with a turnover less than a day should never have to discard used frying oil because of breakdown, except in the case

of product abuse or a contaminant. Operations with a slower turnover rates need to include this product quality and economic factor in their frying oil selection criteria.

Before we move on further, let us recapitulate what we have learnt so far. The salient points are listed in points to remember given herewith. Read them carefully.

POINTS TO REMEMBER

1. Natural fats and oils vary widely in their physical properties even though they are composed of the same or similar fatty acids.
2. Physical properties of a oil or a fat are of critical importance in determining its functional characteristics or use in food products.
3. Performance testing is the means for evaluating the fat or oil's ability to perform the desired functions in a food product.
4. Cake batter aeration can be affected by the plasticity, consistency, emulsification and other properties of fats and oil.
5. Deep fat frying has become one of the most important methods of food preparation.
6. Factors affecting the frying process are frying temperature, oxygen from air, moisture content of the food, duration of frying and presence of contaminants.
7. The rate of frying fat deterioration varies with the food fried, the frying fat utilized, the fryer design and the operating conditions.
8. Fresh oil must be added to the fryer to compensate for the fat removed by the fried product. This addition helps to overcome the changes in the frying fat.
9. Quality and flavour of the frying fat will be maintained at a desired level with the highest turnover rate.

Check your progress Exercise 2

1. Name the factors that affect physical properties of fats and oils.

2. Mention important functional properties of fats and oils

3. What are the salient features of performance test?

4. Name the factors affecting deep fat frying.

5. What is turnover rate of frying oil?

6. How does turn over rate affect the quality of frying oil?

3.6 DETERIORATIVE CHANGES IN FATS AND OILS

From our discussion so far it is clear that the food products undergo changes in flavour due to the chemical changes occurring in fats and oils present in them. The causative factors responsible for such changes are presence of enzymes, atmospheric oxygen and application of high temperature. Lipid oxidation is one of the major causes of food spoilage. It is of great economic concern to the food industry because it leads to the development of various off-flavours and off odours generally called 'rancid' (oxidative rancidity), in edible oils and fat-containing foods, which render these foods less

acceptable. In addition, oxidative reactions can decrease the nutritional quality of food and certain oxidation products are potentially toxic. On the other hand, under certain conditions, a limited degree of lipid oxidation is sometimes desirable, as in aged cheeses and in some fried foods.

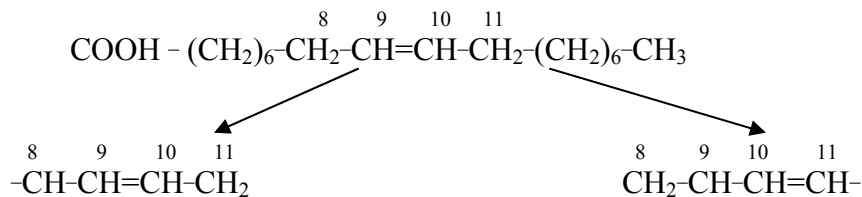
In this section we will look at the oxidative and other changes occurring in fats and oils causing deterioration. We begin with autoxidation.

3.6.1 Autoxidation

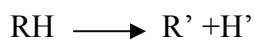
It is generally agreed that “autoxidation”, that is, *the reaction with molecular oxygen via a self – catalytic mechanism*, is the main reaction involved in oxidative deterioration of lipids. Autoxidation reaction can be divided into three parts:

- a. initiation,
- b. propagation, and
- c. termination.

In the initiation part, hydrogen is removed from the fatty acid chain to yield a free radical. The removal of hydrogen takes place at the carbon atom next to the double bond and can be brought about by the action of light, metals etc. Let us understand this concept with the help of an example. For example, in oleic acid, the reaction will proceed by removal of hydrogen from carbons 8 or 11 resulting in free radical as shown herewith.

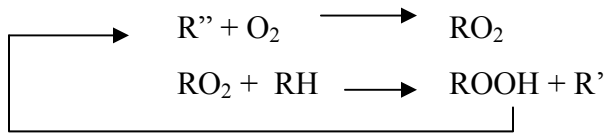


Generally, the reaction can be shown as:

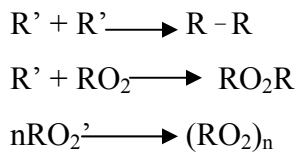


(R' is the free radical)

Once a free radical is formed, it will combine with oxygen to form a peroxy-free radical which can remove hydrogen from another unsaturated molecule who yield a peroxide and a new free radical. This is called 'propagation reaction', as illustrated herewith. This reaction may repeat upto several thousand times and has the nature of a chain reaction.



The propagation can be followed by termination, if the free radicals react with themselves to yield non-active products:



You must remember that the hydro peroxides (ROOH) formed in the propagation part of the reaction are the primary oxidation products. They are generally unstable and decompose into secondary oxidation products which include a variety of compounds. Among the secondary oxidation products, aldehydes and alcohols form an important group. The volatile aldehydes are mainly responsible for the oxidized flavour (rancid) of fats.

A general scheme summarizing the overall picture of lipid autoxidation is given in the figure 3.1.

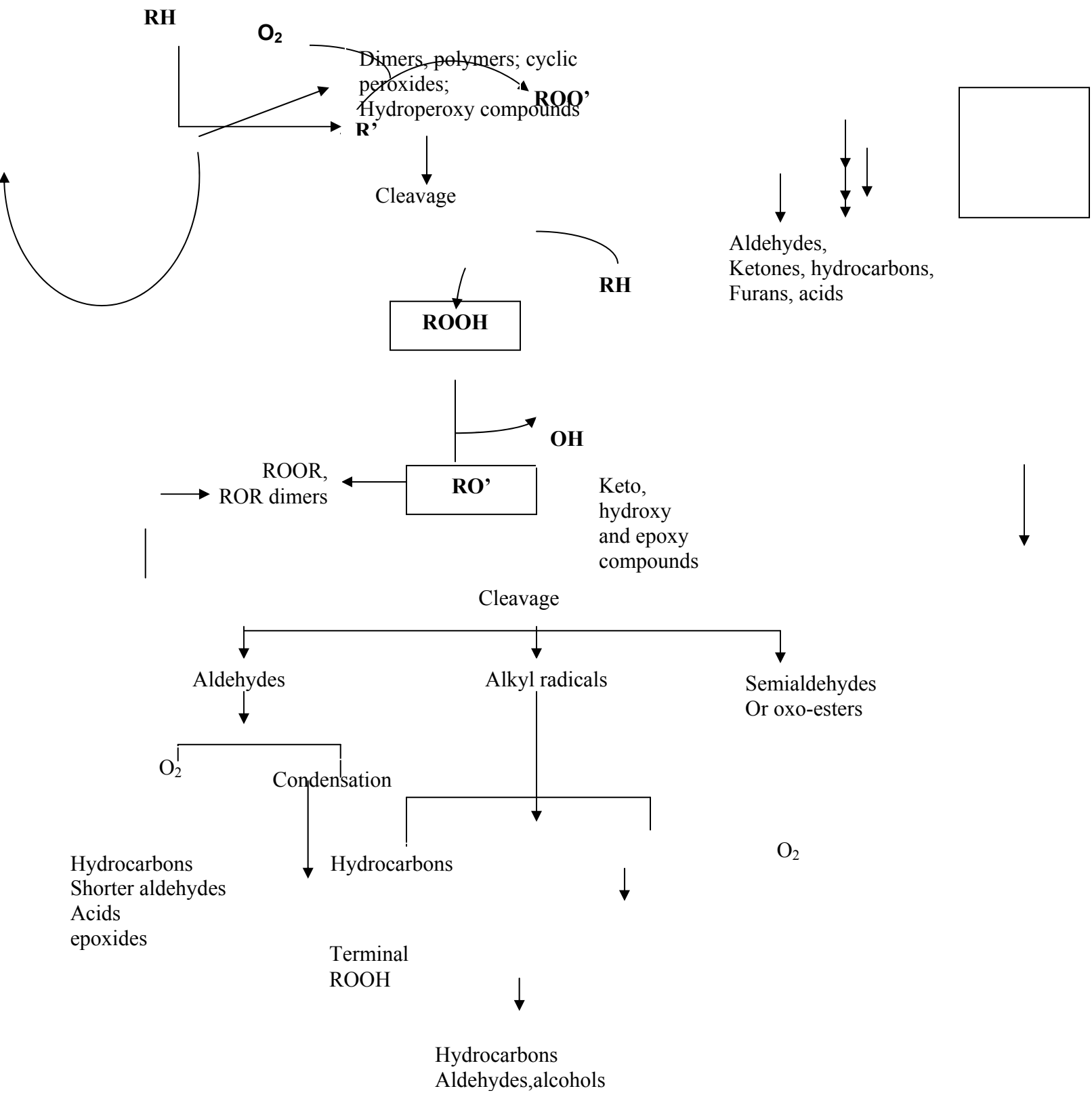


Figure 3.1: Generalised scheme for autoxidation of lipids

There are many factors influencing the lipid autoxidation process you have just learnt about. Let us get to know them.

3.6.2 Factors Influencing Lipid Oxidation

Food lipids contain a variety of fatty acids that differ in chemical and physical properties and also in their susceptibility to oxidation. In addition, foods contain numerous non lipid components that may co-oxidize and / or interact with the oxidizing lipids and their oxidation products. Oxygen concentration, temperature and moisture are the other factors influencing autoxidation. Let us learn how.

- *Fatty acid composition*

We know fats/oils are made up of fatty acids. The number, position and geometry of double bonds within the fatty acids affect the rate of oxidation. Relative rates of oxidation for arachidonic, linolenic, linoleic and oleic acids are approximately 40:20:10:1, respectively. Cis acids oxidize more than their trans-isomers, and conjugated double bonds are more reactive than nonconjugated. Autoxidation of saturated fatty acids is extremely slow. At room temperature, they remain practically unchanged when oxidative rancidity of unsaturates becomes detectable. At high temperatures, however, saturated acids can undergo oxidation at significant rates.

- *Oxygen concentration*

When oxygen is abundant, the rate of oxidation is independent of oxygen concentration, but at very low oxygen concentration, the rate is approximately proportional to oxygen concentration. However, the effect of oxygen concentration on rate is also influenced by other factors, such as temperature and surface area.

- *Temperature*

In general, the rate of oxidation increases as the temperature is increased. Temperature also influences the relation between rate and oxygen partial pressure. As the temperature is increased, changes in oxygen partial pressure have a smaller

influence on the rate because oxygen becomes less soluble in lipids and water, as the temperature is raised.

- *Surface area*

The rate of oxidation increases in direct proportion to the surface area of the lipid exposed to air. Furthermore, as surface – volume ratio is increased; a given reduction in oxygen partial pressure becomes less effective in decreasing the rate of oxidation. In oil-in-water emulsions, the rate of oxidation is governed by the rate at which oxygen diffuses into the oil phase.

- *Moisture*

In model lipid systems and various fat-containing foods, the rate of oxidation depends strongly on water activity. In dried foods with very low moisture contents (a_w values of less than about 0.1), oxidation proceeds very rapidly. Increasing the a_w to about 0.3 retards lipid oxidation and often produces a minimum rate. The protective effect of small amounts of water is believed to occur by reducing the catalytic activity of metal catalysts, by quenching free radicals and / or by impeding access of oxygen to the lipid.

At somewhat higher water activities ($a_w = 0.55 - 0.85$), the rate of oxidation increases again, presumably as a result of increased mobilization of catalysts and oxygen.

- *Pro-Oxidants*

Transition metals, particularly those possessing two or more valency states and a suitable oxidation – reduction potential between them (e.g., cobalt, copper, iron, manganese and nickel), are effective pro-oxidants. If present, even at concentrations as low as 0.1 ppm, they can decrease the induction period and increase the rate of oxidation. Trace amounts of heavy metals are commonly encountered in edible oils and they originate from the soil in which the oil – bearing plant was grown, from the animal, or from metallic equipment used in processing or storage. Trace metals are also naturally occurring components of all food tissues and of all fluid foods of biological origin (eggs, milk, and fruit juices) and are present in both free and bound forms.

After autoxidation, we look at the deteriorative changes caused by lipolysis.

3.6.3 Lipolysis

What do we mean by lipolysis? *Hydrolysis of ester bonds in lipids is called lipolysis.* This may occur by enzyme action or by heat and moisture, resulting in the liberation of free fatty acids. Free fatty acids are virtually absent in the fat of living animal tissue. These can be formed, however, by enzyme action after the animal is killed. Since animal fats are not usually refined, prompt rendering is of particular importance. The temperatures commonly used in the rendering process are capable of inactivating the enzymes responsible for hydrolysis. In contrast to animal fats, oils in mature oil seeds may have undergone a substantial hydrolysis by the time they have harvested, giving rise to significant amounts of free fatty acids. Neutralization with alkali is thus required for most vegetable oils after they are extracted.

Lipolysis is a major action occurring during deep fat frying due to large amounts of water introduced from the food and the relatively high temperatures used. Development of high level free fatty acids during frying is usually associated with foaming and a decrease in the smoke point of the oil and reduction in the quality of the fried food. The release of short – chain fatty acids by hydrolysis is responsible for the development of an undesirable rancid flavour (hydrolytic rancidity) in raw milk. Furthermore, free fatty acids are more susceptible to oxidation than other fatty acids esterified to glycerol.

Lipolysis, therefore, can cause changes in fats and oils which are best avoidable. On the other hand, you would be surprised to learn that certain typical cheese flavours are produced by deliberate action of microbial and milk lipases. Controlled and selective lipolysis is also used in the manufacture of other food items, such as yogurt and bread.

Besides lipolysis, thermal decomposition too can bring about changes in oils and fats which are deteriorative. Let us learn about these changes.

3.6.4 Thermal Decomposition

Heating of food produces various chemical changes, some of which can be important to flavour, appearance, nutritive value and toxicity. Not only do the different nutrients in food undergo decomposition reactions, but these nutrients also interact among themselves in extremely complex ways to form a very large number of new compounds.

The chemistry of lipid oxidation at high temperatures is complicated by the fact that both thermolytic and oxidative reactions are simultaneously involved. Both saturated and unsaturated fatty acids undergo chemical decomposition when exposed to heat in the presence of oxygen. A schematic summary of these mechanisms is shown in figure 3.2.

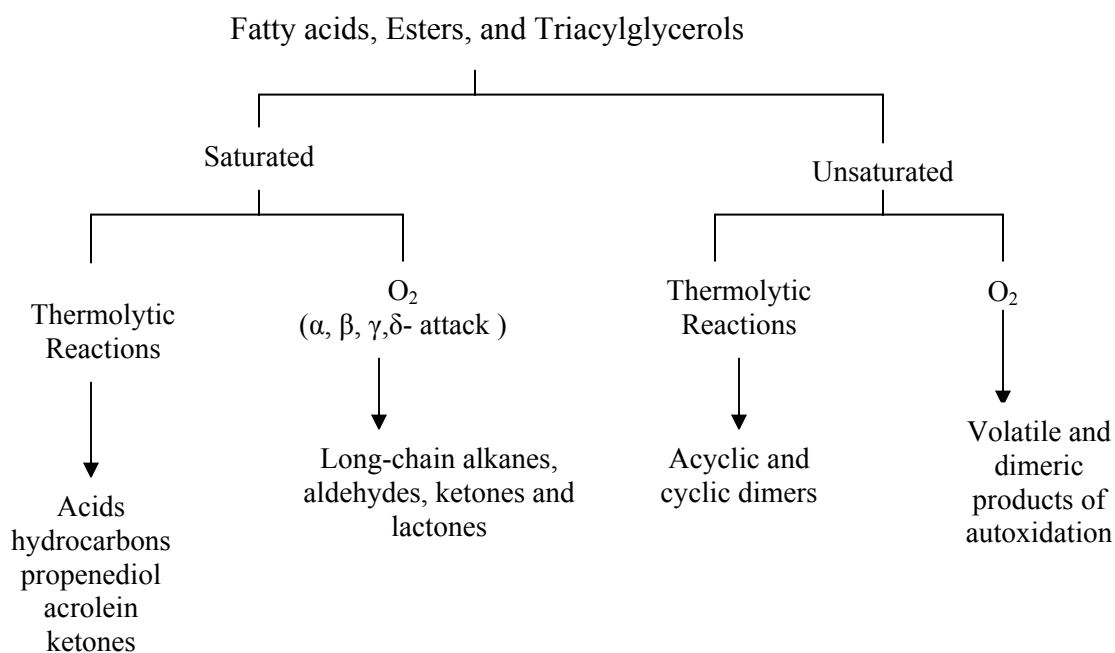


Figure 3.2: Thermal Decomposition of Fats and Oils

With thermal decomposition, we complete our study on the deteriorative changes in fats and oils. Now, the next important issue is how to prevent these deteriorative changes? The answer lies in one word ‘Antioxidants’. Let us learn about what the antioxidants are and how they play a protective role in the context of fats and oils.

3.7 ANTIOXIDANTS

Antioxidants are the substances that can delay onset, or slow the rate of oxidation of autoxidizable materials. By virtue of this property, they provide protection against oxidative changes in fats and oils. They act by reacting with the free radicals and thereby terminate the propagation of chain reaction. The antioxidant reacts with the fatty acid free radical or with the peroxy free radical. Literally hundreds of compounds, both natural (including vitamins C and E, vitamin A, selenium (a mineral) and a group known as the carotenoids) and synthesized, have been reported to possess antioxidant properties. Their use in foods, however, is limited by certain obvious requirements not the least of which is adequate proof of safety. The main lipid soluble antioxidants currently used in food are monohydric or polyhydric phenols with various ring substitutions. For maximum efficiency, primary antioxidants are often used in combination with other phenolic antioxidants or with various metal sequestering agents.

Although the mechanisms by which many antioxidants impart stability to pure oils are relatively well known, much remains to be learned about their action in complex foods. Some commonly used/present antioxidants in fats and oils and their characteristics are discussed herewith.

Characteristics of Some Commonly Used Primary Antioxidants:

- *Tocopherols:* These are the most widely distributed antioxidants in nature, and they constitute the principal antioxidants in vegetable oils. A relatively high proportion of the tocopherols present in crude vegetable oils survives the oil processing steps and remains in sufficient quantities to provide oxidative stability in the finished product.
- *Butylated hydroxyanisole (BHA):* It is commercially available as a mixture of two isomers and has found wide commercial use in the food industry. It is highly soluble in oil and exhibits weak antioxidant activity in vegetable oils, particularly those rich in natural antioxidants. BHA is relatively effective when used in combination with other primary antioxidants. BHA has a typical phenolic odor that may become noticeable if the oil is subjected to high heat.

- *Tertiary Butylhydroquinone (TBHQ)*: TBHQ is moderately soluble in oil and slightly soluble in water. In many cases, TBHQ is more effective than any other antioxidant in providing oxidative stability to crude and refined polyunsaturated oils, without problem of colour or flavour stability. TBHQ is also reported to exhibit good carry - through characteristics in the frying of potato chips.

POINTS TO REMEMBER

1. Lipid oxidation is one of the major causes of food spoilage. It leads to the development of off flavours and off odours generally called rancid.
2. Autoxidation is the reaction of fats and oils with molecular oxygen. It consists of three steps namely, initiation, propagation and termination.
3. Volatile aldehydes formed during autoxidation are mainly responsible for the rancid flavour of fats and oils.
4. The number, position and geometry of double bonds in the fatty acid chain affect the rate of oxidation. As the number of double bonds increase, there is an increase in the rate of oxidation.
5. Oxygen concentration, temperature, surface area of the lipid exposed to air and moisture content influence the lipid oxidation.
6. Hydrolysis of ester bonds in lipids can occur by enzyme action, heat and moisture, resulting in the liberation of free fatty acids.
7. Development of high level of free fatty acids during frying is associated with a decrease in smoke point and reduction in the quality of fried food.
8. Lipid oxidation at high temperature involves both thermolytic and oxidative reactions leading to loss of flavour, appearance and nutritive value.
9. Antioxidants can delay the onset, or slow the rate of oxidation of fats and oils.

Check your progress Exercise 3

1. What is autoxidation and mention the three steps involved in it?

2. What is rancidity? Mention the compounds responsible for it.

3. List the factors influencing lipid oxidation.

4. Define lipolysis and name the compound liberated by it.

5. List the compounds formed by the thermal decomposition of fats and oils.

6. How antioxidants delay the onset of rancidity?

7. Name some commonly used antioxidants.

3.8 LET US SUM UP

Lipids are the major components of oil bearing materials and adipose tissue. They consist of broad group of compounds that are generally soluble in organic solvents. Largest

source of vegetable oil is the seeds of plants such as peanut, sunflower, cottonseed, mustard and safflower. Acylglycerols or glycerol esters of fatty acids which make upto 99% of the lipids of plant and animal origin have been traditionally called fats and oils. Oils of vegetable origin contain large amounts of oleic and linoleic acid. Physical and chemical properties of oils and fats are important to their functional properties in many foods. Many essential attributes contributed by fats and oils can be evaluated by conducting performance tests. These tests are designed for products such as baked goods, candy, coating snacks and formulated products. Deep fat frying is an important method of food preparation. Factors affecting the process of deep fat frying are frying temperature, exposure to air, moisture content of the food being fried, presence of contaminants such as trace metals, soap or detergent and duration of heating. Fats and oils undergo changes in flavour or they develop rancid flavour due to the presence of enzymes, atmospheric oxygen and application of high temperature. Autoxidation is the main reaction involved in the oxidative deterioration of lipids. Autoxidation occurs through free radical mechanism consisting of three steps, namely, initiation, propagation and termination. Lipid oxidation is influenced by the fatty acid composition, oxygen concentration, temperature, surface area, moisture and pro-oxidants. Lipolysis is the hydrolysis of the ester bonds in the lipids resulting in the liberation of free fatty acids which are more susceptible to oxidation than acylglycerols. Lipids undergo chemical decomposition when exposed to heat in presence of oxygen. Antioxidants are the substances that can delay the onset or slow the rate of oxidation of lipids. The main antioxidants used in food are monohydric or polyhydric phenols with various ring substitutes. Tocopherols are the most widely distributed natural antioxidants in vegetable oils. Tertiary butyl hydroquinone (TBHQ) is more effective than any other antioxidant in providing oxidative stability to oils and fats.

3.9 GLOSSARY

Acylglycerols	: Most abundant; these constitute upto 99% of the lipids of plant and animal origin. They are esters of fatty acids with glycerol.
Antioxidants	: Substances that can delay the onset, or slow the rate of oxidative deterioration of oils and fats.
Autoxidation	: Reaction of the molecular oxygen with oils and fats leading to the development of off odour or rancidity.
Cis-trans isomers	: Atoms or groups are called <i>cis</i> or <i>trans</i> to one another when they project respectively on the same or on opposite sides of a reference plane identifiable as common among stereoisomers. The compounds in which such relations occur are termed <i>cis/trans</i> -isomers.
Fatty acids	: Aliphatic monocarboxylic acids that can be liberated by hydrolysis from naturally occurring fats and oils.
Functional property	: Properties of fats and oils which have a marked influence on the preparation and quality of a food product.
Lipids	: Broad group of compounds that constitute the principal structural components of all living cells, and are generally soluble in organic solvents.
Lipolysis	: Hydrolysis of ester bond in lipid caused by enzyme action, heat and moisture resulting in liberation of free fatty acids.
Oleic – linoleic group	: Most abundant group of fats and oils that contain large amounts of oleic and linoleic acid.
Oxidation-reduction Potential (ORP)	: ORP is related to the concentration of oxidizers or reducers in a solution, and their activity or strength. It provides an indication of the solution's ability to oxidize or reduce another material. These chemicals have the ability to oxidize (accept electrons) or reduce (donate electrons) molecules.

Performance test	: A method for evaluating the ability of fat or oil to perform the desired functions in a food product.
Pro-oxidants	: Transition metals, possessing two or more valency states and a suitable oxidation-reduction potential between them.
Rancidity	: Development of off-flavour in fats and oils caused by autoxidation, lipolysis or thermal decomposition.
Thermal Decomposition	: Chemical decomposition of oils and fats when exposed to heat in the presence of oxygen.

3.10 ANSWERS TO CHECK YOUR PROGRESS EXERCISES

Check Your Progress Exercise 1

1. Lipids are a broad group of compounds those are generally soluble in organic solvents but sparingly soluble in water. Main sources of lipids are oil bearing nuts, seeds and fruits. Example peanuts, sunflower, mustard and soyabean.
2. The role of food lipids in human diet are follows: lipids supply calories, essential fatty acids, act as fat-soluble vitamin carriers and increase the palatability of food.
3. The major classes of lipids are simple lipids (acylglycerols and waxes); Compound lipids (glycerophospholipids); Derived lipids (compounds that are not simple or compound lipids) example, Carotenoids and vitamins. Acylglycerols are the glycerol esters of fatty acids which make up to 99% of the lipids of plant and animal origin.
4. Milk fats Example: Cow and Buffalo milk;
Lauric acid group Example: Coconut oil;
Vegetable butters Example: Cocoa butter;
Oleic linoleic acid group Example: Peanut, cotton seed, sunflower oils;

Linolenic acid group Example: Soyabean, Mustard;

Animal fats Example: Lard, tallow

Check Your Progress Exercise 2

1. The factors that affect physical properties of fats and oils are fatty acid composition, degree of unsaturation and structure of individual triglycerides.
2. The important functional properties of fats and oils are discussed as follows. Frying oil is an effective heat exchange medium, to help in development of texture and flavour of fried foods. Form emulsions in batter and dough. Contribute to the texture and flavour of baked products.
3. The salient features of performance test are that it helps in evaluating the ability of fat and oil to perform the desired function in a food product. It is essential for the development of specific food products and formulations.
4. The factors affecting deep fat frying are temperature of frying; presence of oxygen; moisture content of food; presence of contaminants such as trace metals and duration of frying
5. Number of hours required for the addition of fresh frying oil equal to the amount of oil maintained in the fryer is referred to as the turnover rate of frying oil.
6. The turn over rate affects the quality of frying oil by maintaining the flavour at a more desirable level, slowing down oxidative changes occurring in frying fat and minimizing discard of used frying oil.

Check Your Progress Exercise 3

1. Reaction of fats and oils with molecular oxygen by means of a self catalytic mechanism is referred to as autooxidation. The three steps involved are initiation, propagation and termination.
2. Off flavours caused by the chemical changes occurring in fats and oils is referred to as rancidity. The compounds responsible for it are unsaturated aldehydes, ketones, alcohols and acids.
3. The factors influencing lipid oxidation are fatty acid composition, oxygen concentration, temperature, surface area of the lipid, moisture and the presence of pro-oxidants.
4. Lipolysis is the hydrolysis of ester bonds in lipids caused by the action of enzyme, heat or moisture. Free fatty acids are liberated as a result of lipolysis.
5. The compounds formed by the thermal decomposition of fats and oils are acyclic and cyclic dimers, long-chain alkanes, aldehydes, ketones and lactones and hydrocarbons.
6. Antioxidants delay the onset of rancidity by reacting with the fatty acid free radical or with the peroxy free radical and thereby terminate the chain reaction of lipid oxidation.
7. Some commonly used antioxidants are Tocopherols, Butylatedhydroxyanisole and tertiary Butylhydroquinone.