Core Course 12: FOOD CHEMISTRY – I

UNIT 3: Lipids (Part- c)

Dr. DEVAKI. C. S
Assistant Professor
Department of Food Science and Nutrition
Yuvaraja's College (Autonomous)
University of Mysore
Mysore - 570 005

Introduction

In continuation with the first two parts, let us learn about changes observed in fats with the effect of frying, during storage conditions and the preventive measures for auto-oxidation. Let us also know about the processing technologies applied for edible fats and oils and different types of fat mimetics. In earlier units, you learnt about the definition of lipids, followed by classification and the analytical techniques used for evaluation of physical and chemical properties of lipids. In this unit, let us learn the following aspects.

Fat is a principal component of the diet. It adds or modifies flavour, texture and helps in leavening batter and doughs. It also contributes to tenderness, flakiness of the product. It transfers heat to food while frying and prevents sticking of food. Sources of fats and oils may be animal, vegetable, or marine, which may be manufactured in some combination in industrial processing. Oils used in margarines, spreads, dressings, retail bottled oils, as well as frying oils are the largest market segments of edible oils. Fats and oils undergo certain undesirable changes during storage which result in spoilage. The major spoilage of fats and oils is rancidity. Various fat replacements attempt to mimic fat in mouthfeel and perception so that it is good tasting and low fat. Their caloric and cholesterol level are significantly less than fat. As a group, fats and oils should be used sparingly in the diet.

This episode deals with the following important sub headings

- ✓ Effect of frying on fats
- ✓ Changes in fats and oils- rancidity, lipolysis, flavor reversion
- ✓ Technology of edible fats and oils
- ✓ Fat Mimetics

1. Effect of frying on fats:

Frying food with melted fat or oil is a common cooking technique. Frying is a rapid heat transfer method that achieves a higher temperature than boiling or dry heat temperature. The characteristics of fats for frying include that the fat must be colorless, odorless, and bland and have a high smoke point.

Frying of fat decomposes it and causes many changes to take place. Oil decomposes chiefly by four ways **(Table 1)**. They all cause lowering of smoking point and operating temperature of oils.

2. Changes in fats and oils

The stability of a fat or fatty food is important to maintain a fresh taste or odour during storage and use. The stability is related to the composition of the lipid moiety and the changes it is subjected to. The presence of agents causing oxidation (prooxidants) or preventing oxidation (antioxidants) and the methods of storage determine their stability. Vegetable fats are usually more stable than some of the animal fats, even though the total unsaturation of the vegetable oils may be greater, because of the natural antioxidants usually present in them.

2.1 Rancidity

Rancidity is the deterioration (spoilage) of fats and fat-containing foods due to lipid oxidation. Rancid foods and oils develop highly reactive chemicals which produce unpleasant odours and flavours, and destroy nutrients in food. Rancidity is accelerated in highly unsaturated fats and storage conditions conducive to chemical changes.

Rancidity if of two types:

i. **Hydrolytic rancidity**, which involves reaction of fats with water and liberation of free fatty acids,

ii. **Oxidative rancidity**, is a more complex and potentially more damaging reaction. The fat is oxidized and decomposes into compounds with shorter carbon chains such as fatty acids, aldehydes, and ketones. All of these are volatile and contribute to the unpleasant odor of rancid fats.

2.1.1. Hydrolytic rancidity (HR): This is caused by the hydrolysis of the fats into free fatty acids (FFAs) and glycerol by the action of enzymes. The enzyme bring about decomposition of fats. The enzyme lipase is the main cause of HR. It can be prevented through heating of the fat to destroy the enzyme and prevent hydrolysis. Contaminating microorganisms may also produce lipase and these can similarly be destroyed with sufficient heating. Fats may become rancid by HR when the triglycerides react with water **(Figure 1)**.

To avoid this type of rancidity

i. fats should be stored in a cool place
ii. If possible lipases should be inactivated
iii. Fats should be kept away from water
iv. Foods to be fried should be as dry as possible before they are added to hot fat
v. The kind of fat used for frying should be selected based on stability

2.1.2. Oxidative rancidity (OR)

Fats, when in contact with air, react with oxygen producing products with undesirable characteristics. This is known as oxidative rancidity. OR is the predominant type of rancidity. In this process, the unsaturated fatty acids are subjected to oxidative rancidity or autoxidation. The more double bonds there are, the greater the opportunity for addition of oxygen to double bonds. This increases the risk of rancidity. Autoxidation is complex and is promoted by heat, light, certain metals (iron, copper), and enzymes known as lipoxygenases. The mechanism of reaction can be separated into three stages: initiation, propagation, and termination.

i. *The initiation stage of the reaction involves formation of a free radical*.

A hydrogen on a carbon atom adjacent to one carrying a double bond is displaced to give a free radical **(Figure 2)**. There is chemical activity around and in the double bonds. As previously mentioned, this reaction is catalyzed by heat, light, certain metals and lipoxygenases. The free radicals that form are unstable and very reactive.

ii. *The propagation stage follows the initiation stage and involves oxidation of the free radical to yield activated peroxide*.

This in turn displaces hydrogen from another unsaturated fatty acid, forming another free radical. The liberated hydrogen unites with the peroxide to form a hydroperoxide and the free radical can be oxidized **(Figure 3)**. Thus, the reaction repeats, or propagates, itself. Formation of one free radical, therefore, leads to the oxidation of many unsaturated fatty acids. Hydroperoxides are very unstable and decompose into compounds with shorter carbon chains, such as volatile fatty acids, aldehydes, and ketones. These are responsible for the characteristic odor of rancid fats and oils.

iii. *The termination stage of the reaction involves the reaction of free radicals to form nonradical products*.

Elimination of all free radicals is the only way to halt the oxidation reaction.

2.2. Lipolysis: The blood transport lipids to the rest of the body and cells absorb them and utilize for energy. This breakdown of fat to yield energy is called lipolysis.

2.3. Flavor reversion:

Flavor reversion is the change in the flavour of fats prior to rancidity. The refined material develops an objectionable flavour and the edible fats become inedible. The reasons attributed to these changes are:

i. Exposure of ultra violet and visible light.
ii. Heating of the fat.
iii. The presence of oxygen for the reaction to occur
iv. Triglycerides containing linolenic acid are precursors to flavour reversion reaction.
v. Traces of Fe and Cu which catalyse the reactions and act as pro-oxidants.

2.4. Prevention of rancidity

Fats can be protected against the rapid development of rancidity by controlling the conditions of storage. Oxidation can be prevented or delayed by avoiding situations that would serve as catalysts for the reaction.

i. Fats and oils must be stored in a cool dark environment
ii. Vacuum packaging of fat-containing products controls oxygen exposure.
iii. Rays of light catalyse the oxidation of fats. By the use of coloured glass containers that absorb the active rays and fats can be protected against

spoilage. Certain shades of green bottles and wrappers and yellow transparent cellophane wrappers are effective in preventing rancidity.

iv. Fats also must be stored away from metals that could catalyze the reaction. Cooking utensils used must be free of copper or iron.

v. Lipoxygenases should be inactivated

vi. In addition, sequestering agents and antioxidants can be added to fats to prevent autoxidation, increasing keeping quality and shelf life of fats.

vii. Sequestering agents bind metals, thus preventing them from catalyzing autoxidation. Examples of sequestering agents include EDTA (ethylenediaminetetraacetic acid) and citric acid.

viii. Antioxidants help prevent autoxidation with its formation of fatty acid free radicals. Antioxidants prevent rancidity by donating a hydrogen atom to the double bond in a fatty acid and preventing the oxidation of any unsaturated bond. They halt the chain reaction along the fatty acid, which leads to rancidity.

ix. Antioxidants naturally present in the food such as vitamin-C, β-carotene and vitamin E (tocopherol) protect against rancidity.

x. Tocopherols are naturally occurring antioxidants that are present in vegetable oils.

Most antioxidants are phenolic compounds. Those approved for use in foods include BHA (butylated hydroxyanisole), BHT (butylated hydroxytoluene), TBHQ (tertiary-butyl hydroquinone), and propyl gallate. These are all synthetic antioxidants.

Use of antioxidants in foods containing fat increases their keeping quality and shelf life. Examination of food labels reveals that antioxidants are used widely in many food products. Without them, the quality of fat-containing foods would not be as good and off-flavors and odors due to oxidative rancidity would be commonplace.

3. Technology of edible fats and oils

3.1. Refining

The process of refining generally is performed on vegetable oils to reduce the FFA content and to remove impurities. By far the most important and widespread method of refining is the treatment of the fat or oil with an alkali solution. This results in a large reduction of FFAs through their conversion into high specific gravity soaps (**Figure 4**).

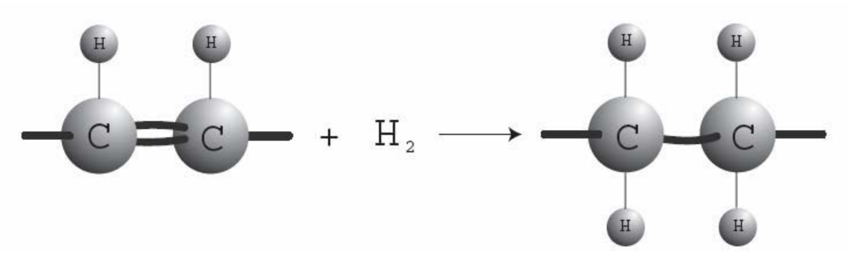
After alkali refining, the fat or oil is water-washed to remove residual soap. The neutralizing agents such as caustic soda, magnesia, lime, carbonate of soda and other alkalis are used for refining.

3.2. Partial Hydrogenation/Hydrogenation

Hydrogenation or hardening is the process of adding hydrogen to unsaturated fatty acids to reduce the number of double bonds. The purpose of hydrogenation is twofold:

a. To convert liquid oils to semisolid or plastic fats for greater utility in certain food uses
b. To increase the thermal and oxidative stability of the fat, and thus the shelf life

Hydrogenation is an important process as it provides the desired stability and functionality to many edible oil products. Hydrogenation of unsaturated fatty acid occurs when hydrogen gas is reacted with oil under controlled conditions of temperature and pressure, and in the presence of a nickel, copper, or other catalyst. The reaction is carefully controlled and stopped when the desired extent of hydrogenation has been reached. Under these conditions, the gaseous hydrogen reacts with the double bonds of the unsaturated fatty acids.



As the reaction progresses, there is a gradual production of trans fatty acids that increases the melting point of the fat/oil and creates a more solid product.

The hydrogenation process is easily controlled and can be stopped at any desired point. If the hydrogenation of cottonseed or soybean oil, for example, is stopped after only a small amount of hydrogenation has taken place, the oils remain liquid. These partially hydrogenated oils are typically used to produce institutional cooking oils, liquid shortenings and liquid margarines.

Further hydrogenation can produce soft but solid appearing fats are used in solid shortenings and margarines. When oils are more fully hydrogenated, many of the carbon to carbon double bonds are converted to single bonds increasing the level of saturation. The resulting product is a hard brittle solid at room temperature.

Processing method: To dry oil, a small amount of very finely divided nickel (catalyst) is added. Other metals may be used, but nickel is the one most widely employed. The oil with nickel is placed in a tight, strong metal vessel and heated. At the same time pure hydrogen gas is forced into it, until a definite pressure is reached. The vessel contains mechanical device to churn up the oil as the gas passes in. Churning helps in proper mixing of hydrogen gas to all the parts of the oil. The process is interrupted when a sample of oil withdrawn from the vessel is found to have desired properties. The oil is then withdrawn and cooled sufficiently and filtered to remove the suspended nickel.

The chief uses of hardened oils are in soap, candles, edible purposes: margarine, chocolate fats, baking-frying and shortening fats. Hydrogenated fats intended for edible purposes must posses the following characteristics:

i. Absence of any objectionable taste and smell
ii. FFAs not exceeding 0.1%
iii. Satisfactory keeping qualities
iv. A texture, consistency and melting point suitable for the particular purpose required.

The hydrogenation conditions can be varied by the manufacturer to meet certain physical and chemical characteristics desired in the finished product. This is achieved through selection of the proper temperature, pressure, time, catalyst and starting oils.

3.3. Interesterification

Interesterification, or rearrangement, causes the fatty acids to migrate and recombine with glycerol in a more random manner. This causes new glycerides to form and increases the heterogeneity of the fat. However, it does not change the degree of unsaturation or the isomeric state of the fatty acids. Hydrogenation may be used in conjunction with interesterification and may either precede or follow it. This gives a shortening manufacturer the ability to produce fats with a wide range of properties.

4. Fat Mimetics

Fat mimetics are substances that imitate organoleptic or physical properties of triglycerides but which cannot replace fat on a one-to-one, gram-for-gram basis. Fat mimetics, often called protein- or carbohydrate-based fat replacers, are common food constituents. They may be chemically or physically modified to mimic the function of fat. The caloric value of fat mimetics ranges from 0–4 kcal/g. Fat mimetics generally adsorb a substantial amount of water. Fat mimetics are not suitable for frying because they bind excessive water and denature or caramelize at high temperatures. Many fat mimetics, however, are suitable for baking and retorting. Fat mimetics are generally less flavorful than the fats. They carry water-soluble flavors but not lipid-soluble flavor compounds.

4.1. Carbohydrate-Based Fat Replacers

Fat replacements may be derived from carbohydrates with 0–4 kcal/g instead of 9 kcal/g. Examples of carbohydrate-based fat replacers (CBFRs) are cellulose, guar gum, locust bean, xanthum gum, gum arabic, pectins, carrageenan, dextrins, maltodextrins and polydextrose. CBFRs have many functional roles in the preparation of food products **(Table 2)**. Starches work well as fat replacements in high-moisture systems to absorb water and form gels that mimic fat. Some CBFRs are used as bulking agents to replace some of the volume lost when fat is omitted. A texture modifier changes the texture of a product to be more like fat.

4.2. Protein-Based Fat Replacers

Microparticulated protein is a reduced-calorie fat replacer, supplying 1-2cals/gram. It is made from the whey in milk or egg protein and is manufactured similarly to modified food starch. Protein-Based Fat Replacers (PBFRs) have many functional roles in the preparation of food products **(Table 2)**. Simplesse is an example, made through a process that gives fat-like textural properties to protein.

Other proteins are heated and blended at high speed to produce tiny protein particles that feel creamy to the tongue. PBFRs cannot be used as substitutes for oils and other fats in frying.

5. Conclusion:

Fat is a principal component of the diet. Frying is a rapid heat transfer method that achieves a higher temperature than boiling or dry heat temperature. Fats and oils may be modified by hydrogenation, inter-esterification. The deterioration of fats and oils occurs as they absorb odors or become rancid. Hydrolytic rancidity releases FFAs and oxidative rancidity produces shorter, off-odor free radicals catalyzed by heat, light, metals, or enzymes. Prevention of oxidation by avoiding catalysts in the environment or by the addition of sequestering agents or antioxidants may be useful in extending shelf life. Foods may contain reduced-fat, low-fat, or no-fat formulations using a variety of fat replacers derived from carbohydrates or proteins. Fats and oils should be used sparingly in the daily diet.

Table 1: Ways of Oil Decomposition

Sl.No	Process	Cause	Changes
1.	Pyrolysis (thermal breakdown)	Heating oil with or without contact with food	Breakdown in molecular structure. Fats → FAs + glycerol → FFAs+acrolein. Irritation by acrolein.
2.	Oxidation	Hot oil surface+oxygen in presence of air	Molecular breakdown. Rancidity develops as and when the oil is heated
3.	Hydrolysis	Water evolved from boiling food+oil	Decomposition of oil by water
4.	Food residues	Food residues+reheated oil	Chemical changes in the residues as well as the reheated oil.

Table 2: Selected Applications and Functions of Fat Replacers

Specific Application	Fat Replacer	General Functions
Baked goods	CBFRs	Retain moisture, retard staling
	PBFRs	Texturize
Salad dressing	CBFRs	Increase viscosity, provide mouthfeel, texturize
	PBFRs	Texturize, provide mouthfeel
Frozen desserts	CBFRs	Increase viscosity, texturize, thicken
	PBFRs	Texturize, stabilize
Margarine, shortening, spreads, butter	CBFRs	Provide mouthfeel
	PBFRs	Texturize
Confectionery	CBFRs	Provide mouthfeel, texturize
	PBFRs	Provide mouthfeel, texturize
Processed meat products	CBFRs	Increase water holding capacity, texturize, provide mouthfeel
	PBFRs	Texturize, provide mouthfeel, water holding
Dairy products	CBFRs	Increase viscosity, thicken, aid gelling, stabilize
	PBFRs	Stabilize, emulsify
Soups, sauces, gravies	CBFRs	Thicken, provide mouthfeel, texturize
	PBFRs	Texturize
Snack products	CBFRs	Texturize, aid formulation
	PBFRs	Texturize

Source: AKOH; A Publication of the Institute of Food Technologists, Expert Panel on Food Safety and Nutrition

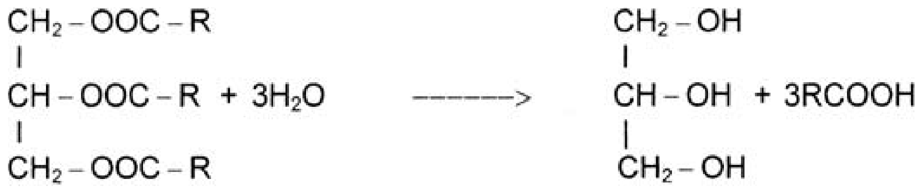


Figure 1: Chemical reaction of Hydrolytic Rancidity

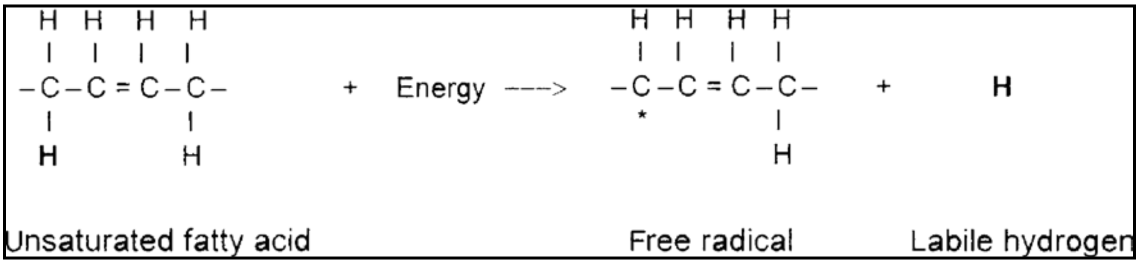


Figure 2: Initiation stage of the free radical formation

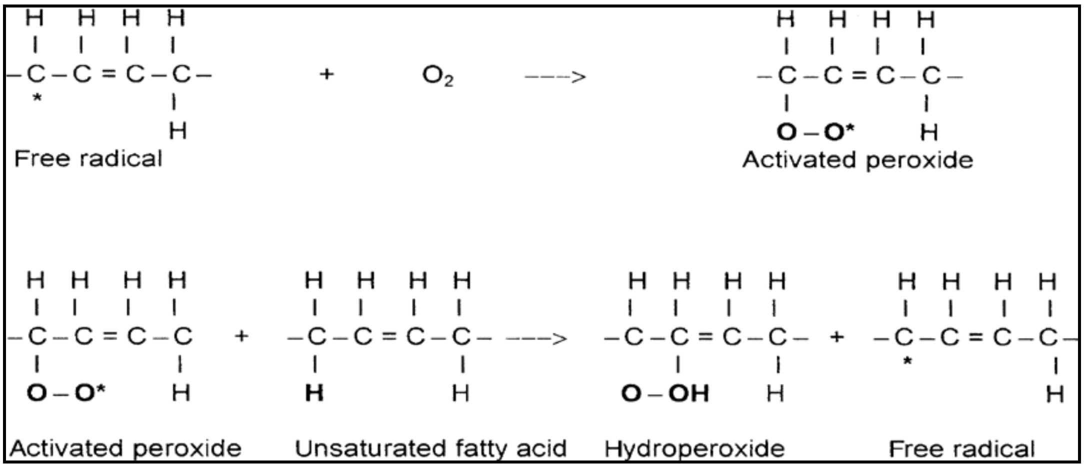
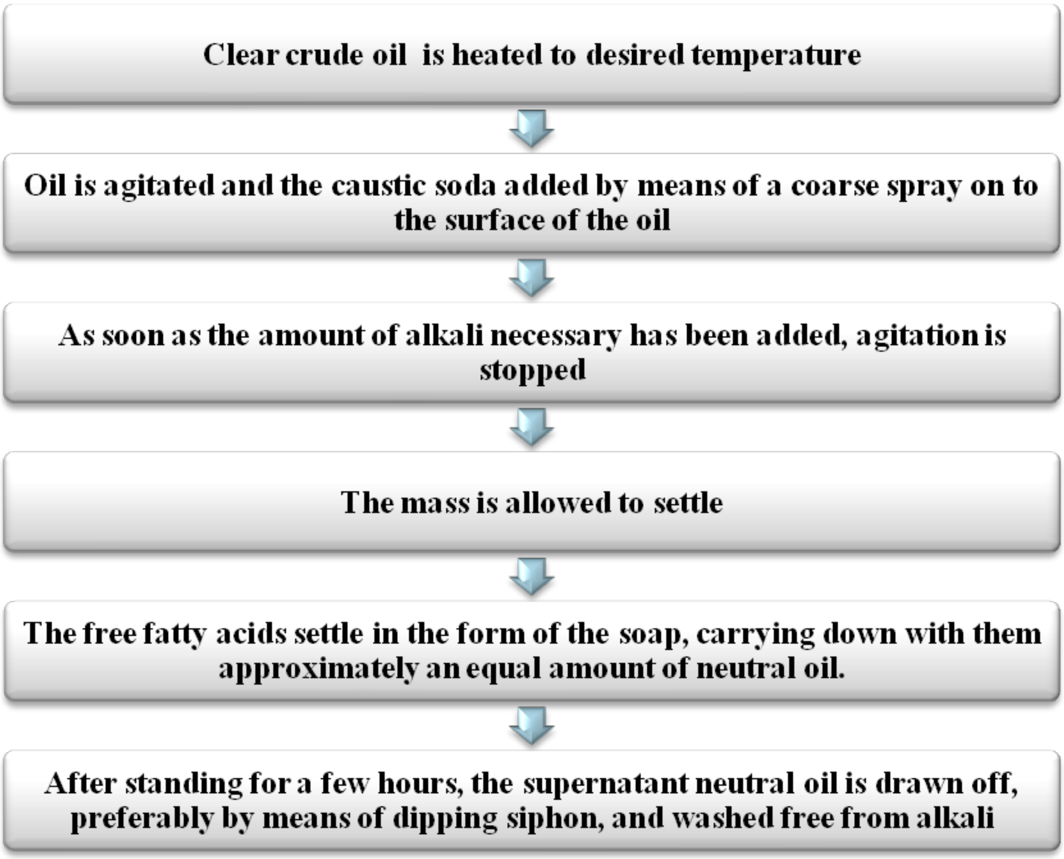


Figure 3: The two reactions of the propagation stage of autoxidation



Clear crude oil is heated to desired temperature

Oil is agitated and the caustic soda added by means of a coarse spray on to the surface of the oil

As soon as the amount of alkali necessary has been added, agitation is stopped

The mass is allowed to settle

The free fatty acids settle in the form of the soap, carrying down with them approximately an equal amount of neutral oil.

After standing for a few hours, the supernatant neutral oil is drawn off, preferably by means of dipping siphon, and washed free from alkali

Figure 4: Process of Refining