

CHAPTER 4

EDIBLE OILS, FATS AND WAXES

CHAPTER 4 OBJECTIVES

- INTRODUCTION
- FATTY ACIDS
- GLYCERIDES
- PHYSICAL PROPERTIES OF TRIGLYCERIDES
- CHEMICAL PROPERTIES OF TRIGLYCERIDES
- SOURCES OF EDIBLE OILS AND MAIN FATS
- OILS AND FATS-PROCESSING AND REFINING
- OILS AND FATS STABILITY AND ANTIOXIDANTS
- METHODS OF ANALYSIS AND TESTING OF OILS AND FATS

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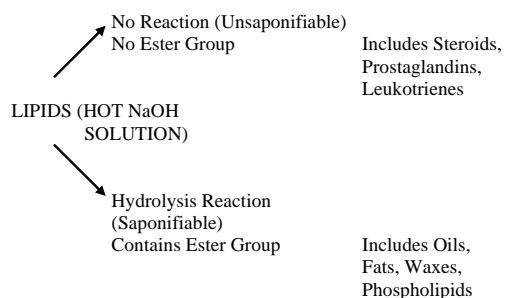
INTRODUCTION

- Fats, oils and waxes are the naturally occurring esters of long straight-chain carboxylic acids.
- They belong to the "Saponifiable" group of lipids. Lipids are biologically produced materials which are relatively insoluble in water but soluble in organic solvents (benzene, chloroform, acetone, ether, etc.).
- The saponifiable lipids contain an ester group and react with hot sodium hydroxide solution undergoing hydrolysis (saponification):

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INTRODUCTION

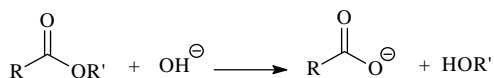


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INTRODUCTION

- What is Saponification? Ester is heated with aqueous alkali (sodium hydroxide) to form an alcohol and the sodium salt of the acid corresponding to the ester. The sodium salt formed is called a soap.



- Fats and oils are esters of glycerol, the simplest triol (tri-alcohol), in which each of the three hydroxyl groups has been converted to an ester.

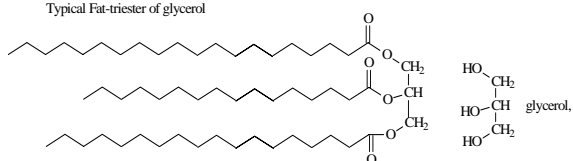
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INTRODUCTION

- The acid portion of the ester linkage (fatty acids) usually contains an even number of carbon in an unbranched chain of twelve to twenty four carbon atoms.
- The triesters of glycerol fats and oils are also known as triglycerides.

Typical Fat-triester of glycerol



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INTRODUCTION

- **The difference between fats and oils is merely one of melting point:** fats are solid at room temperature (20°C) while oils are liquids. Both classes of compounds are triglycerides.
- Since glycerol is common to all fats and oils, whether animal or vegetable, it is the fatty acid part of the fat (oil) that is of interest.
- The differences among triglycerides (fats and oils) are due to the length of the hydrocarbon chains of the acids and the number of position of double bonds (unsaturation).

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INTRODUCTION

- The hydrocarbon chains of the fatty acids may be completely saturated (a saturated fat) or may contain one or more double bonds.
- The geometric configuration of the double bond in fats and oils is normally *cis*.
- If the chain includes more than one double bond, the fat is called **polyunsaturated**.
- The presence of a double bond puts a “kink” in the regular zig-zag arrangement characteristics of saturated carbons.

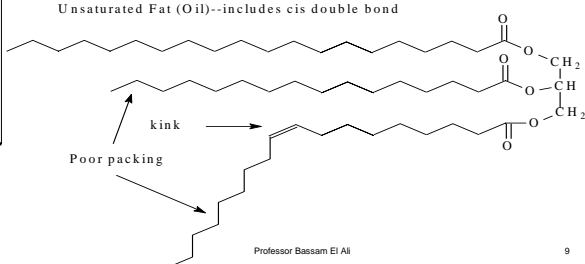
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INTRODUCTION

- Therefore, the molecules cannot form a neat, compact lattice and tend to coil, so unsaturated triglycerides often melt below room temperature and are thus classified as oils.

Unsaturated Fat (Oil)--includes cis double bond



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INTRODUCTION

- Fats and oils are the most concentrated source of energy. They provide approximately 9 Kcal of energy per gram, compared to 4 Kcal/g for proteins and carbohydrates.
- They are carriers of fat-soluble vitamins and essential fatty acids.
- They also contribute to food flavor and mouth feel as well as to the sensation of product richness.
- They are used as frying fats or cooking oils where their role is to provide a controlled heat-exchange medium as well as to contribute to color and flavor.

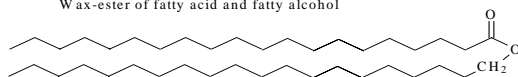
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INTRODUCTION

- Waxes are monoesters of long-chain fatty acids, usually containing 24 to 28 carbon atoms, with long-chain fatty primary alcohols.
- A fatty alcohol has a primary alcohol group (-CH₂OH) attached to a 16 to 36 carbon atoms long chain. Waxes are normally saturated and are solids at room temperature.

Wax-ester of fatty acid and fatty alcohol

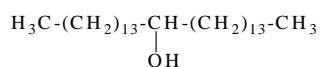


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INTRODUCTION

- Plant waxes are usually found on leaves or seeds (cabbage leaf wax consists of the primary alcohols C₁₂ and C₁₈-C₂₈ esterified with palmitic acid and other acids).
- The dominant components are stearyl and ceryl alcohol (C₂₆H₅₃OH). In addition to primary alcohols, esters of secondary alcohols, e.g., esters of nonacosane-15-ol are present:



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INTRODUCTION

- Waxes can be classified according to their origins as naturally occurring or synthetic.
- The naturally occurring waxes can be classified into animal, vegetable and mineral waxes. The vegetable waxes include carnauba, ouricouri and candelilla.
- Petroleum waxes are the most prominent mineral waxes. Paraffin wax is petroleum wax consisting mainly of normal alkanes with molecular weights usually less than 450.

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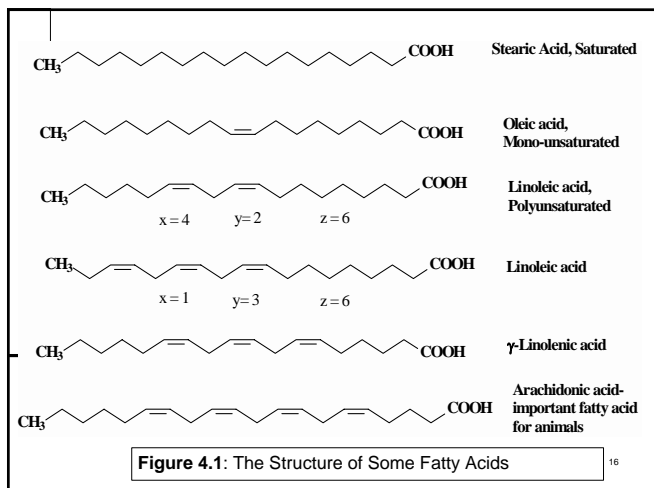
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FATTY ACIDS

- Fatty acids: carboxylic acids obtained from the hydrolysis of a fat or oil. They are the building blocks of the triglycerides.
- The fats and oils are often named as derivatives of these fatty acids.
- Normal saturated fatty acids have a long, linear hydrocarbon chain having a general formula $\text{CH}_3(\text{CH}_2)_n\text{COOH}$ (where n is even= 2 to 24).
- The unsaturated fatty acids may have one double bond (monosaturated) or have more than one cis-methylene double bond (polyunsaturated).

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FATTY ACIDS

- Fatty The following three systems of nomenclature are in use for naming fatty acids.
 - > The common (trivial) names.
 - > The number of carbon atoms in the chain.
 - > The International Union of Pure and Applied Chemistry (IUPAC) system.
- The trivial names which indicate the initial source of fatty acids, are used more often than the IUPAC names in the industry.
- For example: butyric acid is a major component of butter flavor; palmitic acid comes from palm kernel; and oleic acid is from olives.

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FATTY ACIDS

- Abbreviation to designate fatty acids: number of carbon atoms in the chain, followed by a colon and additional numbers indicating number of double bonds.
- The 18-carbon series: C18:0 (stearic acid), C18:1 (oleic acid), C18:2 (linoleic acid) and C18:3 (linolenic acid).
- One or two letter abbreviations are also used, and these four acids sometimes are designated by St, O, L and Ln, respectively.

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FATTY ACIDS

- When double bonds are present, the suffix “anoic” is changed to “enoic”, “dienoic”, or “trienoic” to indicate the **number** of bonds present.
- **The location** of the first carbon in the double bond is indicated by a number preceding the IUPAC systematic name.
- **The geometric** configuration of the double bonds is indicated by the latin prefixes “cis-“ (both hydrogens on one side) and “trans-“ (hydrogen across from each other).
- Unsaturation between the 9 and 10 carbons with “cis” orientation is most common in polyunsaturated fatty acids.
- Accordingly, oleic, linoleic and linolenic acids are called 9-octadecenoic, 9,12-octadecadienoic and 9,12,15-octadecatrienoic acids, respectively.

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FATTY ACIDS

Carbon Atoms	Common Name	Systematic Name	Common Sources
Saturated Fatty Acids			
3	Propionic	Propanoic	Bacterial fermentation
4	Butyric	Butanoic	Milk fats
5	Valeric	Pentanoic	Bacterial fermentation
5	Isovaleric	3-Methylbutanoic	Dolphin and porpoise fats
6	Caproic	Hexanoic	Milk fats, some seed oils
8	Caprylic	Octanoic	Milk fats, Palmae seed oils
10	Capric	Decanoic	Ship and goat milk, palm
12	Lauric	Dodecanoic	seed oils, sperm head oil
14	Myristic	Tetradecanoic	Coconut-oil
16	Palmitic	Hexadecanoic	Palm and coconut oils
18	Stearic	Octadecanoic	Palm oil

Table 4.2 Some Important Fatty Acids, their Names and Common Sources

FATTY ACIDS

Carbon Atoms	Common Name	Systematic Name	Common Sources
Unsaturated Fatty Acids			
10	Caproleic	9-Decenoic	Milk fats
10	Stillingic	2,4-Decadienoic	Stillingia oil
12	Lauroleic	2-Dodecenoic	Butterfat
18	Linolenic	9,12,15-Octadecatrienoic	Linseed oil

Table 4.2 Some Important Fatty Acids, their Names and Common Sources

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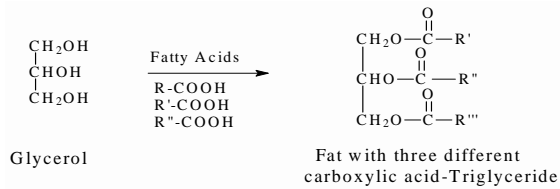
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GLYCERIDES

- Glycerol can be esterified commercially with one, two or three fatty acids to produce mono-, di-, or triglycerides.
- Fats and oils are naturally occurring triglycerides.
- The properties of triglycerides depend on the fatty acid composition and on the relative location of fatty acids on the glycerol.



GLYCERIDES

Table 4.3: Triglyceride Types and Isomeric Forms of Natural Fats

	Types (% Wt)				Isomers (% Wt)			
	GS ₃	GS ₂ U	GSU ₂	GU ₃	SUS	SSU	USU	UUS
Pig fat (Lard)	2.5	22.4	55.7	19.4	1.0	21.4	46.9	8.8
Peanut oil	0.1	9.9	42.5	47.5	9.3	0.6	0.7	41.8
Beef fat (Tallow)	12.6	43.7	35.3	8.4	30.6	13.1	3.4	31.9
Cocoa butter	7.1	67.5	23.3	2.1	65.0	2.5	0.2	23.1
Soybean oil	0	3.7	31.0	65.3	3.7	0	0	31.0

GS₃: a fully saturated glyceride; GS₂U: a glyceride composed of two saturated acids and one unsaturated acid. Distinguishing between the 1, 3 and 2 positions permits identification of the SUS and SSU isomers of GS₂U and the USU and UUS isomers of GSU₂.

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GLYCERIDES

PHYSICAL PROPERTIES OF TRIGLYCERIDES

- The physical properties, such as melting points, specific heat, viscosity, density and refractive index, depend on:
 - the type of fatty acids present in the triglyceride and their location,
 - chain length of fatty acids,
 - number and location of *cis* and *trans* double bonds on the fatty acid chains.

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GLYCERIDES

PHYSICAL PROPERTIES OF TRIGLYCERIDES

- **Melting Point**
 - The melting range of fats depends on the triglyceride composition.
 - Melting points increase with chain length.
 - *Trans* fatty acids always have higher melting points than their *cis* counterparts for any chain length.
 - Melting point data are useful in animal fats and processed fats but are of little value for vegetable oils since most oils are liquids at ambient temperatures.

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GLYCERIDES

PHYSICAL PROPERTIES OF TRIGLYCERIDES

■ Specific Heat

- The specific heat of fats is defined as the **ratio of the heat capacity of a fat to the heat capacity of water**, or **the quantity of heat required for a one-degree temperature change** in a unit weight of fats.
- Specific heat does increase with increasing unsaturation of fatty acids in both the liquid and solid states of a fat. Liquid fats have almost twice the specific heat values than those of solid fats.

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GLYCERIDES

PHYSICAL PROPERTIES OF TRIGLYCERIDES

■ Viscosity

- Viscosity of the fatty acids increases with chain length and decreases with increasing unsaturation.
- There is an approximately linear relationship between **log** viscosity and temperature.
- The viscosity of oils usually increases in prolonged heating due to polymerization (gum formation).

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GLYCERIDES

PHYSICAL PROPERTIES OF TRIGLYCERIDES

■ Density

- The density of fats and oils is an index of the weight of a measured volume of the material.
- The solid fat index (SFI) is related approximately to the percentage of solids in a fat at a given temperature.
- When SFI is determined at a number of specified temperatures, it can be especially useful to margarine manufacturers or other processors.

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GLYCERIDES

PHYSICAL PROPERTIES OF TRIGLYCERIDES

■ Refractive Index

- The refractive index of fats and oils is sensitive to composition.
- The refractive index of a fat increases with increasing chain length of fatty acids in the triglycerides or with increasing unsaturation.
- The refractive index can be utilized as a control procedure during hydrogenation processes.

GLYCERIDES

PHYSICAL PROPERTIES OF TRIGLYCERIDES

■ Polymorphism

- **Polymorphism:** the existence of a substance in two or more forms, which are significantly different in physical or chemical properties.
- Certain pure or mixed fatty acid triglycerides may show as many as five different melting points. Each crystal system has a characteristic melting point, x-ray diffraction pattern and infrared spectrum.
- For example, tristearin can exist in three polymorphic forms with melting points of 54.7°C, 63.2°C and 73.5°C.
- Polymorphism has several industrial implications in use of fats as shortenings, margarines and cocoa butter.

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GLYCERIDES

CHEMICAL PROPERTIES OF TRIGLYCERIDES

- The most important chemical reactions for triglycerides (fats and edible oils) are hydrolysis, methanolysis and interesterification.
- The other reactions: hydrogenation, isomerization, polymerization and autoxidation.

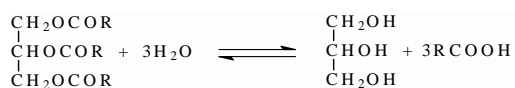
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CHEMICAL PROPERTIES OF TRIGLYCERIDES

Hydrolysis

- The fat or oil can be hydrolyzed into fatty acids and glycerol by treatment with steam under elevated pressure and temperature.
- The reaction is reversible and is catalyzed by inorganic catalysts (ZnO, MgO or CaO) and an acid catalyst (aromatic sulfonic acid).



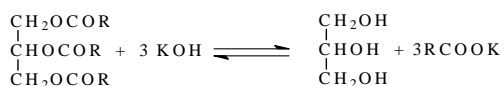
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CHEMICAL PROPERTIES OF TRIGLYCERIDES

Hydrolysis

- Glycerides can also be hydrolyzed by treatment with alkali (saponification).
- After acidification and extraction, the free fatty acids are recovered as alkali salts (soaps).



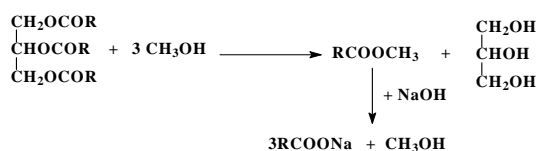
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CHEMICAL PROPERTIES OF TRIGLYCERIDES

Methanolysis

- The fats and oil reacts with methanol to produce fatty methyl esters.
- Inorganic alkali, quaternary ammonium salts, and enzymes (lipase) have been used as catalysts for methanolysis in commercially practiced processes for soap manufacture.



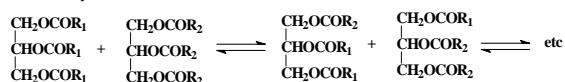
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CHEMICAL PROPERTIES OF TRIGLYCERIDES

Interesterification

- Interesterification causes a fatty acid redistribution within and among triglyceride molecules.
- Substantial changes in the physical properties of fats and oils or their mixtures without altering the chemical structure of the fatty acids.
- The reaction is very slow even at 200-300°C, but the rate of reaction can be accelerated by using sodium methylate.



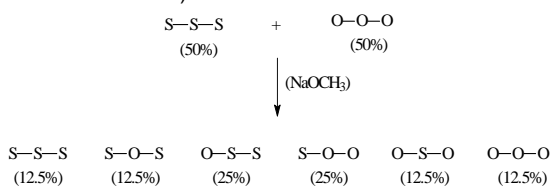
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CHEMICAL PROPERTIES OF TRIGLYCERIDES

Interesterification

- Interesterification may be either random or directed.
- In *random interesterification* the acyl groups are randomly distributed (equal proportions of tristearin (S-S-S) and triolein (O-O-O) are allowed to interesterified).



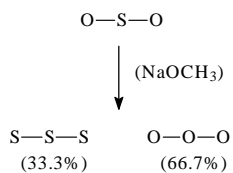
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CHEMICAL PROPERTIES OF TRIGLYCERIDES

Interesterification

- In *directed interesterification*, the reaction temperature is lowered until the higher melting and least soluble triglyceride molecule in the mixture crystallize
→ higher and lower melting fractions.



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CHEMICAL PROPERTIES OF TRIGLYCERIDES

Hydrogenation

- The unsaturated double bonds in fatty acid chain are converted to saturated bonds by addition of hydrogen.
- Suitable solid catalyst: nickel, platinum, copper, or palladium.
- Hydrogenation is exothermic, and leads to an increase in melting point and drop in iodine value.
- Partial hydrogenation can lead to isomerization of *cis* double bonds (geometrical isomerization).

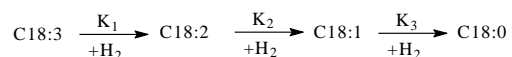
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CHEMICAL PROPERTIES OF TRIGLYCERIDES

Hydrogenation

- Polyunsaturated fatty acids such as linolenic acid (C18:3) is hydrogenated more quickly to linoleic (C18:2) or oleic acid (C18:1) than linoleic to oleic acid or oleic acid to stearic acid (C18:0).



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CHEMICAL PROPERTIES OF TRIGLYCERIDES

Isomerization

- The configuration of the double bond in naturally occurring fatty acids, present in oils and fats, is predominantly in the cis form.
- Isomerization can occur if oils and fats are heated at temperatures above 100°C in the presence of bleaching earths or catalysts such as nickel, selenium, sulfur or iodine.

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CHEMICAL PROPERTIES OF TRIGLYCERIDES

Polymerization

- Under deep frying conditions (200-300°C) the unsaturated fatty acids undergo polymerization reactions forming dimeric, oligomeric and polymeric compounds.
- The rate of polymerization increases with increasing degree of unsaturation: saturated fatty acids are not polymerized.
- In thermal polymerization polyunsaturated fatty acids are first isomerized into conjugated fatty acids.
- Conjugated fatty acids interact by Diels-Alder reactions producing cyclohexene derivatives.

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CHEMICAL PROPERTIES OF TRIGLYCERIDES

Autoxidation

- Fats and oils often contain double bonds.
- Autoxidation of a fat or oil yields a mixture of products that include low molecular weight carboxylic acids, aldehydes and methyl ketones.
- The autoxidation reactions involve three steps: initiation, propagation, and termination.
- The initiation step leads to the formation of a hydroperoxide on a methylene group adjacent to a double bond; this step proceeds via a free-radical mechanism.

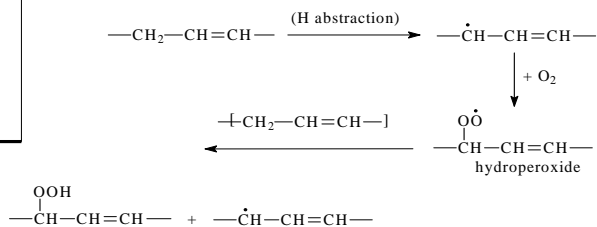
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CHEMICAL PROPERTIES OF TRIGLYCERIDES

Autoxidation

- The second step, which is also a reaction in the propagation cycle, is the addition of another molecule to the hydroperoxide radical to generate new free radicals.



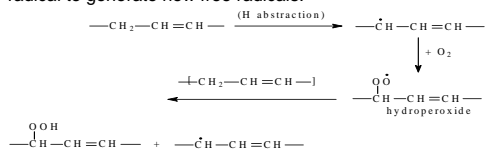
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CHEMICAL PROPERTIES OF TRIGLYCERIDES

Autoxidation

- The second step, which is also a reaction in the propagation cycle, is the addition of another molecule to the hydroperoxide radical to generate new free radicals.



- The chain length of these two radical-reaction steps is about 100. When the radical concentration has reached a certain limit, the chain reaction is gradually stopped by mutual combination of radicals, **the termination step**.

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SOURCES OF EDIBLE OILS AND MAIN FATS

- The organ fats of domestic animals, such as cattle and hogs and milk fat are important raw materials for fat production.
- The edible oils are mostly of plant origin. Olive oil and palm oil are extracted from the fruits.
- All other oils are extracted from the oilseeds.
- World oilseed production in 2000 was 307.7 million tons.

SOURCES OF EDIBLE OILS AND MAIN FATS

- Soybeans constitute the largest share (56%) and the United States are the main crop growers.
- Malaysia grows mainly palm oil.
- The Philippines grows coconut.
- China, Europe, India and Canada grow rapeseed (canola). Sunflower is grown in the United States, Australia, Europe and Argentina.
- The cottonseed market is dominated by the United States, China, Pakistan, India and the former Soviet Union.

SOURCES OF EDIBLE OILS AND MAIN FATS

- World vegetable oil consumption in 2000 was 87.2 million tons. United States consumption was 7.39 million tons.
- In the United States market animal fats (tallow and lard) have a relatively small share (4%) as compared to vegetable oils.
- The consumption of four oils-soybean (80%), corn (4%), canola (4%) and cottonseed (3%) have grown rapidly over the past 30 years as compared with the traditional oils and animal fats.

OILS AND FATS – PROCESSING AND REFINING

- Crude fats and oils consist primarily of glycerides.
- They also contain many other lipids in minor quantities. Corn oil, for example, may contain glycerides plus phospholipids, glycolipids, many isomers of sitosterol and stigmasterol (plant sterols), several tocopherols (vitamins E), vitamin A, waxes, unsaturated hydrocarbons, as well as many products of decomposition, hydrolysis, oxidation and polymerization of any of the natural constituents.

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OILS AND FATS – PROCESSING AND REFINING

- All crude oils and fats obtained after rendering, crushing or solvent extraction, inevitably contain variable amounts of non-glyceridic co-constituents like:
 - fatty acids,
 - partial glycerides (mono- and diglycerides),
 - phosphatides,
 - sterols,
 - hydrocarbons,
 - pigments (gossypol, chlorophyll), vitamins (carotene),
 - sterol glucosides, protein fragments, traces of pesticides and "heavy" metals.

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OILS AND FATS – PROCESSING AND REFINING

- The general methods employed to produce edible oils suitable for human consumption consist of:
 - (a) seed preparation
 - (b) extraction
 - (c) degumming
 - (d) neutralization
 - (e) bleaching
 - (f) deodorization
 - (g) hydrogenation and sometimes winterization.

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OILS AND FATS – PROCESSING AND REFINING

Seed Preparation

- When oils seeds, which are received at the oil mill, contain plant residues, damaged seeds, dust, sand, wood, pieces of metal and foreign seeds.
- The oils seeds are carefully cleaned of these materials using magnets, screens, and aspirator systems.
- The cleaned seeds are dried to remove moisture. Next, the dried oil-seeds are usually decorticated to remove the hull that surrounds the oilseed *meat* before being further processed.
- Hulls always contain much less oil than do the kernels or meats.

OILS AND FATS – PROCESSING AND REFINING

Extraction

- The raw material for the fat and oil industry comes from the animals (hogs, sheep and fatty fish); fleshy fruits (palm and olive); and various oilseeds.
- Most oilseeds are grown specifically for processing to oils and protein meals.
- The purpose of oil extraction is two fold.
- Firstly is to extract the maximum amount of good quality oils and then to get maximum value from the residual press cake or meal.
- The following three methods, with varying degree of mechanical simplicity are used: (1) rendering (2) pressing with mechanical presses and (3) extracting with a volatile solvent.

OILS AND FATS – PROCESSING AND REFINING

Extraction

- The following three methods, with varying degree of mechanical simplicity are used:
 1. rendering
 2. pressing with mechanical presses, and
 3. extracting with a volatile solvent.

OILS AND FATS – PROCESSING AND REFINING

Extraction-Rendering

- The fatty tissues are chopped into small pieces and are boiled in steam digesters.
- The fat is gradually liberated from the cells and floats to the surface of the water, where it is collected by skimming.
- A similar method is used in the extraction of palm oil from the fresh palm fruits.

OILS AND FATS – PROCESSING AND REFINING

Extraction-Pressing

- Oil seeds do not have fat cells like those of animals for storing fats. Instead oil is stored in microscopic globules throughout the cells.
- The general sequence of modern operations in pressing oilseeds and nuts is as follows.
 1. Preparation of the seed to remove stray bits of metals and removal of hulls;
 2. Reduction of particle size of the kernels (meats) by grinding;
 3. Cooking and pressing in hydraulic or screw presses.

OILS AND FATS – PROCESSING AND REFINING

Extraction-Pressing

- Oil expressed without heating contains the least amount of impurities and is often of edible quality without refining or further processing.
- Such oils are known as cold-drawn, cold-pressed, or virgin oils.
- The expressed oil from cooked seeds contains greater quantities of nonglyceride impurities such as phospholipids, color bodies and unsaponifiable matter.
- **Such oils are more highly colored and are not suitable for edible use.**

OILS AND FATS – PROCESSING AND REFINING

Extraction-Solvent Extraction

- The press cake emerging from a screw press still retains 3 to 15 percent of residual oil.
- More complete extraction is done by solvent extraction of the residues obtained from mechanical pressing.
- The common solvent for edible oil is commercial hexane or heptane, commonly known as petroleum ethers.
- After extraction, maximum solvent recovery is necessary for economical operation.
- The solvent is recovered by distillation and is reused. The extracted oil is mixed with prepress oil for refining. The extracted meals contain less than 1 percent of residual oil.

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OILS AND FATS – PROCESSING AND REFINING

Refining (Degumming and Neutralization)

- Degumming reduces mainly the phosphatides and metals content of the crude oil by mixing it with an acid and water.
- The phosphatides are present in free hydratable form (HP) or in non-hydratable form (NHP), mostly in combination with some Ca^{++} , Mg^{++} or Fe^{++} .
- In alkali refining, the NHP which remain behind in the oil after acid treatment, and the free fatty acids formed during the hydrolysis (lipolysis) of the HP, are further removed by neutralization.
- Degumming consists of treating the oil with a small amount (0.05%) of concentrated phosphoric acid and water, followed by centrifugal separation of coagulated material (lecithin).

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OILS AND FATS – PROCESSING AND REFINING

Refining (Degumming and Neutralization)

- The process is applied to many oils (e.g. soya bean oil) that contain phospholipids in significant amounts.
- Refining with alkali removes free fatty acids which are formed during the lipolysis of the fat or oil before rendering or extraction.
- The oil is treated with an excess of 0.1% caustic soda solution and the mixture is heated to about 75°C to break any emulsions formed.
- The mixture is allowed to settle. The settlings, called "foots", are collected and sold as "soapstock".

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OILS AND FATS – PROCESSING AND REFINING

Refining (Degumming and Neutralization)

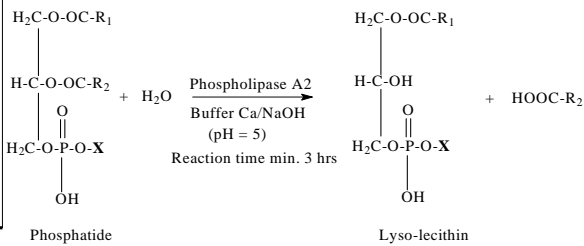
- After the oil has been refined, it is usually washed with water to remove traces of alkali and soapstock.
- After water washing, the oil may be dried by heating in a vacuum or by filtering through a dry filter and material.
- In the Enzymatic degumming process, part of the hydratable phosphatides are enzymatically modified by removing the fatty acid on the C-2 position of the glycerol, using a phospholipase A2 enzyme as biocatalyst. These modified phosphatides facilitate the removal of the remaining NHP.

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OILS AND FATS – PROCESSING AND REFINING

Refining (Degumming and Neutralization)



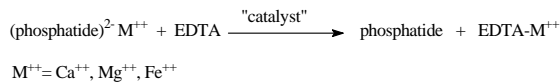
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OILS AND FATS – PROCESSING AND REFINING

Refining (Degumming and Neutralization)

- In the soft degumming process, a chelating agent (EDTA) is added to the oil to remove the cations from the non-hydratable phosphatides.



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OILS AND FATS – PROCESSING AND REFINING

Refining (Degumming and Neutralization)

Table 4.10- Example of Enzymatic Degumming

Rapeseed Oil	Crude Oil	Degummed Oil
Phospholipids	0.6%	0.01-0.02%
P	240 ppm	4-8 ppm
H ₂ O	0.1%	0.3%

Note: P-content = phosphatide content x 10⁴/25

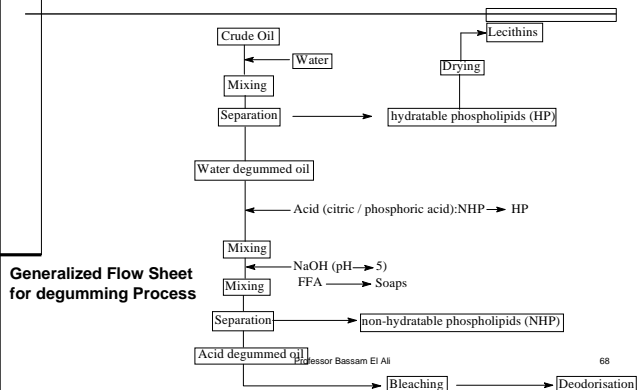
Table 4.11- Example of Soft Degumming

Soybean Oil	Crude Oil	Degummed Oil
Phospholipids	0.3%	0.01%
P	120 ppm	3-5 ppm
Ca	59	0.1
Mg	35	0.02
Fe	1.6	0.04

Note: P-content = phosphatide content x 10⁷/25

OILS AND FATS – PROCESSING AND REFINING

Refining (Degumming and Neutralization)



OILS AND FATS – PROCESSING AND REFINING

Refining (Degumming and Neutralization)

- The refined oils are usually dark in color due to the presence of some pigmented materials such as chlorophyll or carotenoids and minor impurities like residual phosphatides, soaps, metals and oxidation products.
- Bleaching reduces the color by absorbing these colorants on bleaching earth (bentonite clays) and/or activated charcoal.
- Bleaching clay also absorbs suspended matter and other minor impurities.

OILS AND FATS – PROCESSING AND REFINING

Refining (Degumming and Neutralization)

- Natural bleaching clays are aluminum silicates, containing relatively high amounts of Mg, Ca or Fe.
- The clays are generally activated by heat treatment.
- The high metal content limits the adsorptive activity of these clays.
- The metals can be removed from the reactive spots by means of acid treatment, yielding clays with much higher adsorptive capacity.

OILS AND FATS – PROCESSING AND REFINING

Refining (Degumming and Neutralization)

- In some cases active carbon is added in the course of bleaching to improve the removal of blue and green pigments as well as polycyclic aromatic hydrocarbons.
- Due to high cost and high oil retention, active carbon is used only in specific cases (e.g. coconut and palm kernel oil), in combination with bleaching clays, mostly in a ratio of 1/10 to 1/20.
- Bleaching is by far the most expensive process in refining in terms of utilities cost.

OILS AND FATS – PROCESSING AND REFINING

Deodorization

- Most fats and oils, even after refining, have characteristic flavors and odors due to the presence of minor amounts of free fatty acids, aldehydes, ketones and other compounds.
- The concentration of these undesirable substances, found in most oils, is generally low, between 0.2 and 0.5%.
- The efficient removal of undesirable substances depend on
 - the vapor pressure of the different minor compounds,
 - the deodorizing conditions (temperature, pressure, residence time),
 - the amount of stripping steam and
 - the geometry of the vessel.

OILS AND FATS – PROCESSING AND REFINING

Hydrogenation

- Hydrogenation is used to convert liquid fats to plastic fats, thereby making them suitable for the manufacture of margarine or shortening.
- Hydrogenated oils and fats also exhibit improved oxidative stability and color.
- Close control of hydrogenation results in highly specific results. For example, salad and cooking oils can be improved by controlled hydrogenation.
- The most unsaturated fatty acid groups are most easily hydrogenated.

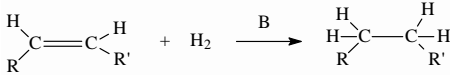
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OILS AND FATS – PROCESSING AND REFINING

Hydrogenation

- Raney nickel-type and copper-containing catalysts are normally used.
- Variables affecting hydrogenation include the catalyst, temperature, hydrogen pressure and amount of agitation.
- The catalytic hydrogenation is frequently accompanied by isomerization with a significant increase of melting point, caused, for example, by **oleic (cis) isomerizing to oleic (trans) acid**.
- The **trans** isomers are much higher melting than natural cis forms



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OILS AND FATS – PROCESSING AND REFINING

Winterization

- Winterization is an operation that consists in removing from certain oils the components that solidify at low temperatures and therefore a source of turbidity or settling in the bottle.
- The process consists in filtering cooled oil under strict control.
- Winterizing is not practiced so widely in hot countries and its application is restricted mainly to sunflower, maize, cotton, olive, ricebran and partially hydrogenated soybean oils.
- A winterized oil should remain clear for at least 24 hrs at 0°C. This corresponds to a wax content of below 50 ppm.

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CHAPTER 4 OBJECTIVES

- INTRODUCTION
- FATTY ACIDS
- GLYCERIDES
- PHYSICAL PROPERTIES OF TRIGLYCERIDES
- CHEMICAL PROPERTIES OF TRIGLYCERIDES
- SOURCES OF EDIBLE OILS AND MAIN FATS
- OILS AND FATS-PROCESSING AND REFINING
- OILS AND FATS STABILITY AND ANTIOXIDANTS
- METHODS OF ANALYSIS AND TESTING OF OILS AND FATS

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FATS AND OILS STABILITY AND ANTIOXIDANTS

- Fats and oil stability: the capability of a fat, oil, or fatty food to maintain a fresh taste and odor during storage and use.
- The ester linkages of triglycerides can be subjected to hydrolysis liberating free fatty acids (lipolysis), or may undergo oxidation forming peroxides and aldehydes (oxidation).
- Lipolytic spoilage is known as *lipolytic rancidity*, or *hydrolytic rancidity*.
- Lipolysis can occur from chemical, enzymatic, or thermal stress actions.

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FATS AND OILS STABILITY AND ANTIOXIDANTS

- Fats and oils also can become rancid due to oxidation and this oxidative spoilage is known as *oxidative rancidity*.
- Lipolytic rancidity usually poses less of a flavor problem than oxidative rancidity.
- Oxidation of fats and oils is the major cause by which the ester linkages of triglycerides in polyunsaturated oil deteriorate.
- The reaction of oxygen with unsaturated fatty acids in fats and oils proceeds through a **free-radical chain reaction mechanism** involving three stages: (1) initiation-formation of free radicals; (2) propagation-free-radical chain reaction; (3) termination-formation of nonradical products.

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FATS AND OILS STABILITY AND ANTIOXIDANTS

- Hydroperoxides are the major initial reaction products of fatty acids with oxygen.
- The initiation step is the removal of weakly held methylene hydrogen to produce an allylic radical $RH \rightarrow R\cdot + H\cdot$, while oxygen adds to the double bond to form a diradical.



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FATS AND OILS STABILITY AND ANTIOXIDANTS

- During propagation, the chain reaction is continued by $R\cdot + O_2 \rightarrow ROO\cdot$ and $ROO\cdot + RH \rightarrow ROOH + R\cdot$ and hydroperoxides, and new hydrocarbon radicals.
- The new radical formed then contributes to the chain by reacting with another oxygen molecule.
- Termination occurs when the radicals interact as follows:
 - $R\cdot + R\cdot \rightarrow RR$
 - $ROO\cdot + R\cdot \rightarrow ROOR$ Non radical products
 - $ROO\cdot + ROO\cdot \rightarrow ROOR + O_2$

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FATS AND OILS STABILITY AND ANTIOXIDANTS

- Trace metals, especially copper, catalyze autoxidation by reacting with hydroperoxides to create new free radicals and initiate new chain reactions.
 - $M^+ + ROOH \rightarrow RO\cdot + OH^- + M^{2+}$ (metal ion is oxidized)
 - $M^{2+} + ROOH \rightarrow ROO\cdot + H^+ + M^+$ (metal ion is reduced)
 - $2 ROOH \rightarrow RO\cdot + ROO\cdot + H_2O$: Net reaction
- Citric acid is often added as a metal sequestrant to effectively inactivate trace metal ions.
- Antioxidants are used to stabilize fats and fat-containing products against oxidation and thereby prolong their stability and storage time.

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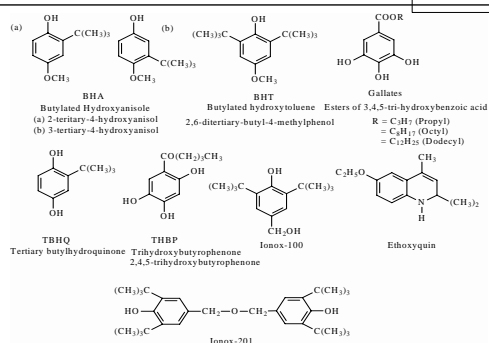
FATS AND OILS STABILITY AND ANTIOXIDANTS

- An antioxidant (AH) acts as free radical traps to terminate oxidation chain reactions:
 - $R\cdot + AH \rightarrow RH + A\cdot$
 - $RO\cdot + AH \rightarrow ROH + A\cdot$
 - $ROO\cdot + AH \rightarrow ROOH + A\cdot$
 - $R\cdot + A\cdot \rightarrow RA$
 - $RO\cdot + A\cdot \rightarrow ROA$
- The major food grade synthetic antioxidants used include butylated hydroxytoluene (BHT), tertiary butylhydroquinone (TBHQ), propyl gallate (PG), and 2, 4,5-tri hydroxy butylphenone (THBP).

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FATS AND OILS STABILITY AND ANTIOXIDANTS



Structures of some synthetic antioxidants

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METHODS OF ANALYSIS AND TESTING OF FATS AND OILS

Identification and Compositional Analysis

- Gas chromatography of fatty acids and the HPLC of triglycerides are used to estimate the selected functional groups or calculate the oils or fats contents.

Saponification Number (SN)

- This is the weight of KOH (in mg) needed to hydrolyze a one-gram sample of an oil or fat.
- The higher the SN, the lower the average molecular weight of the fatty acid in the triglycerides.

METHODS OF ANALYSIS AND TESTING OF FATS AND OILS

Identification and Compositional Analysis

Acid Value (AV)

- This value is important for determination of free fatty acids (FFA) in crude and refined oils and fats.
- It is the number of milligrams of KOH needed to neutralize the organic acids present in 1 g of oil or fat.
- FFA is calculated as free oleic acid and reported as a percentage. The AV is determined by multiplying % FFA with a factor of 1.99.

METHODS OF ANALYSIS AND TESTING OF FATS AND OILS

Identification and Compositional Analysis

Table 4.12- Iodine (IN) and Saponification Numbers (SN) of Various Edible Fats and Oils

Oil/Fat	IN	SN
Coconut	256	9
Palm Kernel	250	17
Cocoa	194	37
Palm	199	55
Olive	190	84
Peanut	192	156
Rapeseed	225	30
Sunflower	190	132
Soya	192	134
Butter	225	30

**METHODS OF ANALYSIS AND TESTING OF
FATS AND OILS**

Identification and Compositional Analysis

Hydroxyl Number (OHN)

- This number reflects the content of hydroxy fatty acids, fatty alcohols, mono- and diacylglycerols and free glycerol.

Color Reactions

- The Halphen test for detecting cottonseed oil is one example.
- This test estimates the presence of cottonseed oil in vegetable or animal fats or oils as the result of a pink color formed between the reagent (sulfur and carbon disulfide) and cyclopropenoic fatty acids normally present in cottonseed oil.

**METHODS OF ANALYSIS AND TESTING OF
FATS AND OILS**

Identification and Compositional Analysis

Composition of Fatty Acids

- The saturated and unsaturated fatty acids with 8 to 24 carbon atoms in animal fats, vegetable oils, marine oils and fatty acids are quantitatively determined by gas chromatography (GC) after conversion to their methyl ester forms.
- Free fatty acid analysis is also possible by using specially selected stationary solid phases. A capillary gas liquid chromatographic method is also used to measure fatty acid composition and levels of trans unsaturation and cis, cis methylene-interrupted unsaturation of vegetable oils.

**METHODS OF ANALYSIS AND TESTING OF
FATS AND OILS**

Identification and Compositional Analysis

Physical Tests for identification

- Specific density, index of refraction, color, viscosity and melting point tests are used to identify fats and oils.
- The Solid Fat Index (SFI) estimates the percent of solids in a semisolid fat on the basis of changes in volume with temperatures. This is of importance in fat hydrogenation and interesterification processes.

**METHODS OF ANALYSIS AND TESTING OF
FATS AND OILS**

Quality Control Tests

Lipolysis

- Free fatty acids (FFA) results from lipolysis (hydrolysis) of oils and fats. This is determined by the FFA or Acid Value.
- The crude oils and animal fats usually have a FFA content exceeding 1%.
- The FFA content is lowered to less than 0.1% by the refining of oil or fat.

**METHODS OF ANALYSIS AND TESTING OF
FATS AND OILS**

Quality Control Tests

Peroxide Value

- The method for determination of peroxide concentration is based on the reduction of the hydroperoxide group with HI (or KI) to liberate free iodine, which may be titrated.
- The peroxide value is expressed in terms of a milliequivalent of iodine formed per kilogram of fat.

**METHODS OF ANALYSIS AND TESTING OF
FATS AND OILS**

Quality Control Tests

Shelf Stability Test

- Shelf life prediction is determined by Active Oxygen Method (AOM).
- The fat or oil is subjected to an accelerated oxidation test under standardized conditions so that the signs of deterioration are revealed within several hours or days.
- The sample is heated at 97.8°C while air is blown through it. The AOM Value is reported as the number of hours to reach a peroxide value of 100 meq/kg.

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