Fats and Oils Technology
Lecture 2

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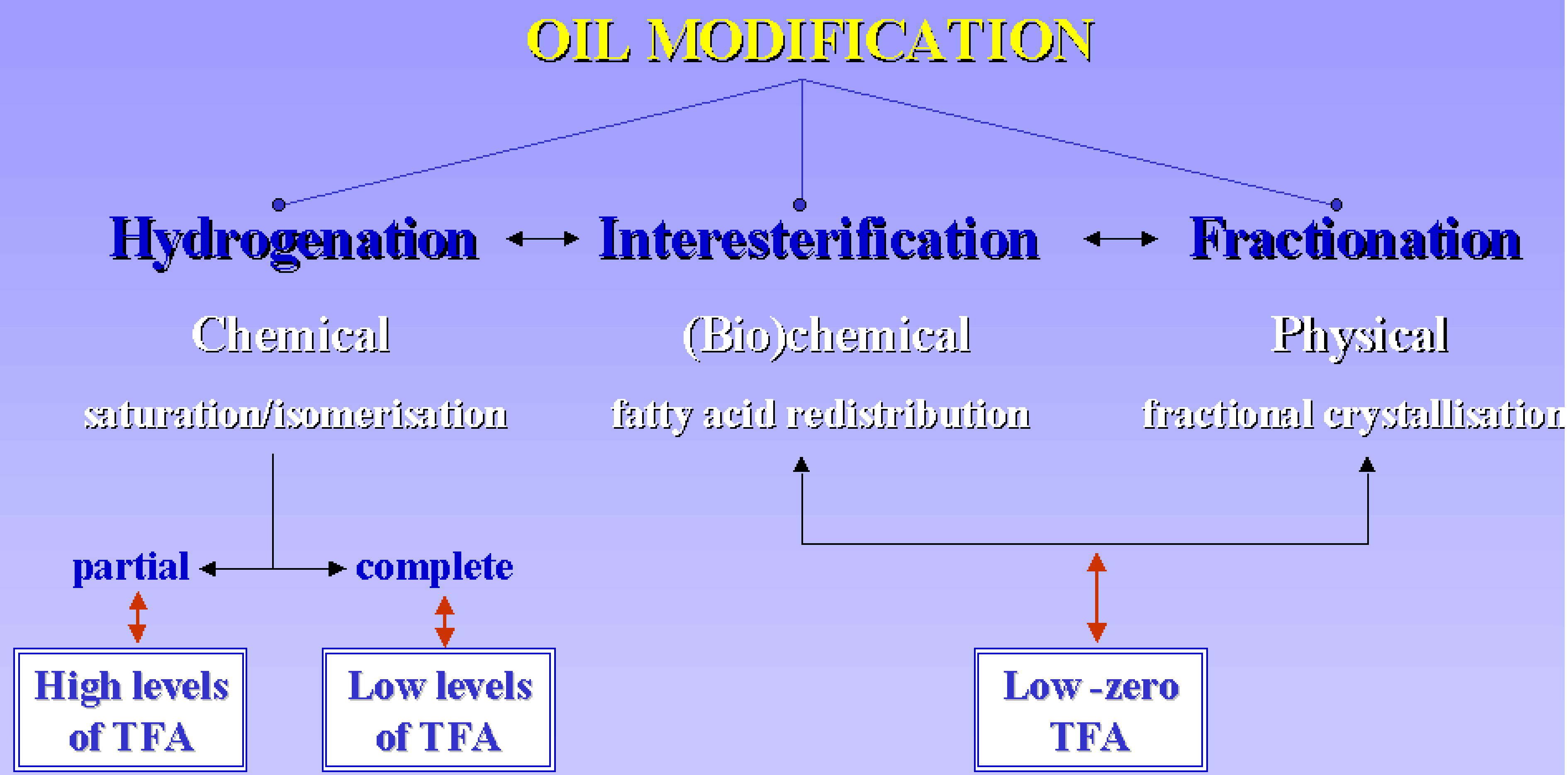
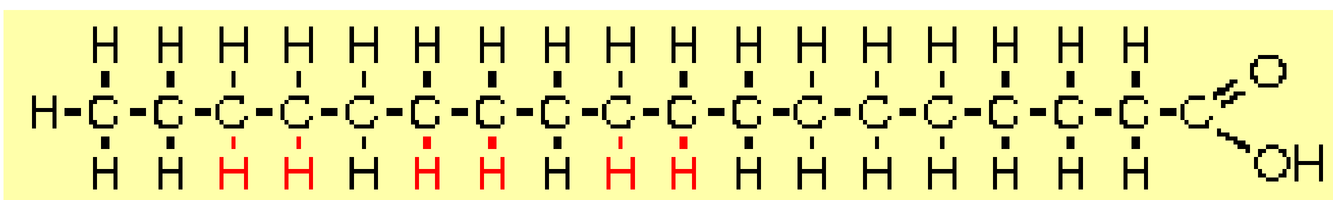

OIL MODIFICATION
Hydrogenation
Interesterification
Fractionation
Chemical
(Bio)chemical
Physical
saturation/isomerisation
fatty acid redistribution
fractional crystallisation
partial
complete
High levels of TFA
Low levels of TFA
Low -zero TFA

Hydrogenation

In the presence of hydrogen and a suitable catalyst the double bonds of unsaturated fatty acids are readily hydrogenated, a reaction at modern margarine manufacture. This is done with hydrogen gas under pressure with a metal catalyst at high temperatures.



The objectives of hdyrogenation are:

- To impart oxidative stability to the oil
- To convert a liquid vegetable or fish oil to a fat with “butter – like” consistency by reducing the degree of unsaturation of its component fatty acids.

Hydrogenated oils or fats have a consistency that is ideal for use as margarine or shortening components.

HOW IT IS DONE:

- **The oils are exposed to hydrogen gas at high pressure and temperatures (2-10 atm, 140-225°C) in the presence of 0.01-0.2% finely divided nickel, and agitated.**

- **The reduction of double bonds is "selective". The ones furthest from ester links of triglycerides and those belonging to the more unsaturated fatty acids are most reactive.**

- **First trienoic acids (with 3 double bonds) are converted to dienoic acids; and then dienoic acids(2 double bonds) to enoic(1double bond) acids.**

Hydrogenation Selectivity of Catalysts

Definitions of "HydrogenationSelectivity":

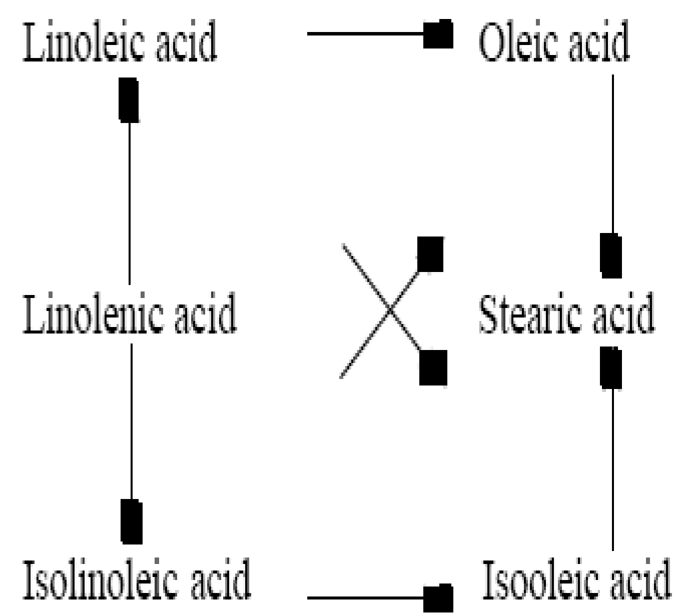
1. **"Preferential hydrogenation of more unsaturated acids with minimum formation of completely saturated fatty acids"**
2. **"The ratio of the rate of hydrogenation of linoleic acid to that of oleic acid"**

Commonly observed selectivities range from 4:1 to 50:1.

In Very selective hydrogenation:

Linoleic acid : Oleic acid ratio is (50 : 1)

Highly selective catalysts are more desirable in the industry.



Hydrogenation process requires the following:

1. High temperatures

2. A metal catalyst such as nickel, zinc, copper, or other reactive metals

3. Hydrogen gas

- The hydrogen gas which is bubbled up through the oil

- The catalyst mixture reacts with carbon atoms of the unsaturated fatty acids and converts them into saturated fatty acids by flipping one of the attached hydrogen molecules and rotating it half the diameter of the carbon chain.

- This effectively creates a new molecular shape resulting in a stiffer or more rigid material, hence the change from a liquid to a semi-solid or solid substance. This new shape stiffens with the hydrogenation process making the oil behave more like a fully saturated fat (such as coconut fat which is 92% saturation and solid at room temperature).

SUMMARY:

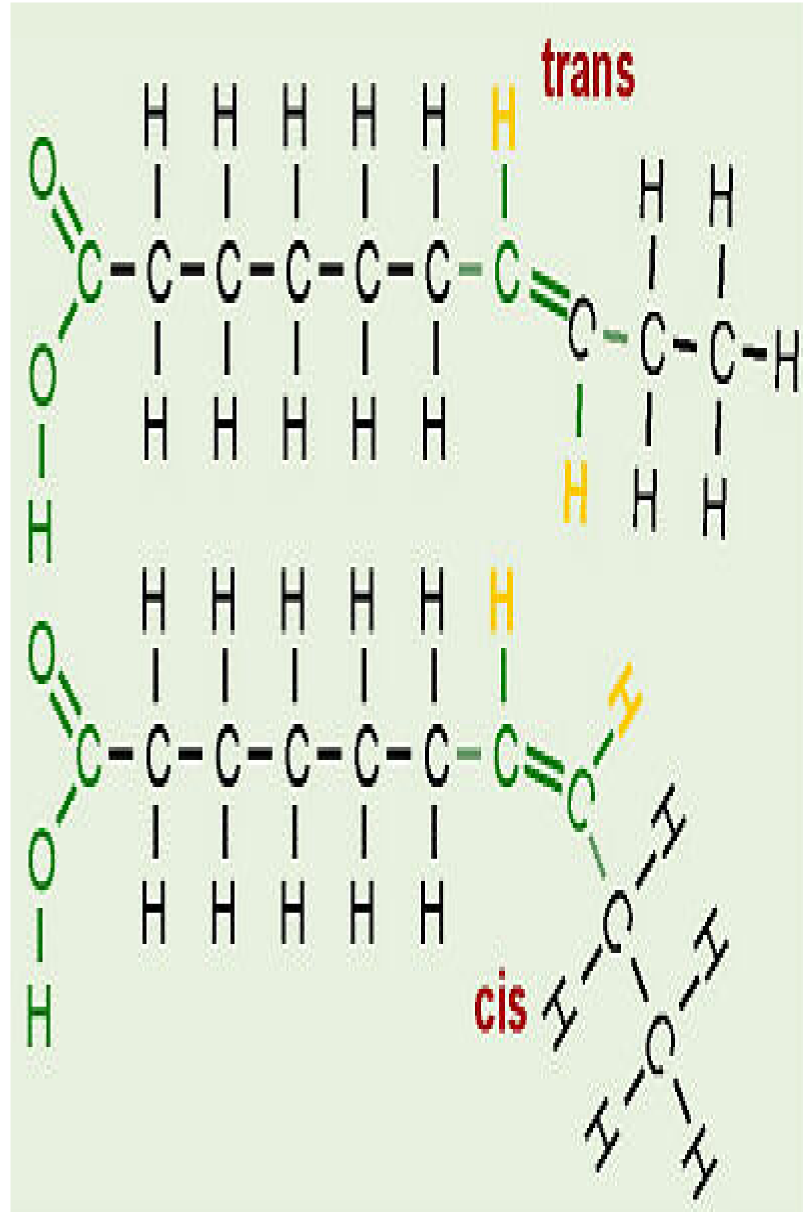
The effects of hydrogenation: Increased Oxidative Stability , Decreased Color; Decreased VitaminA; Isomerization(trans f.a.)

Hydrogenation and Trans fats

Trans fats are formed as a result of hydrogenation reaction

- **Hydrogenation raises the melting point of the fat and retards rancidity. But as recent health studies have found, other problems can ensue when consuming large amounts of trans fats from hydrogenated products.**
- **Trans Fatty Acid**
  The hydrogen molecules attached at the center of the fatty acid carbon chain flips 180 degrees, which straightens the natural curve or kink in the typical cis-configured fat.

- When hydrogenated, the cis-shape chemically alters to a trans configuration and hence is called a “trans” fat. Most margarine and vegetable shortening have been trans fat converted through full or partial hydrogenation process. Trans fats interfere with metabolic absorption efficiencies and tend to congregate at adipose tissue sites.
- On July 23, 2003: A decree was passed which states that , as of January 1, 2006, food manufacturers will be required to label the trans-fat content of their foods on all nutritional fact labels.



Hydrogenation

Margarine Production

- Margarine is a “water in oil” emulsion prepared from suitable “margarine oil” stocks and a “milk phase”.
- The emulsion is modified by the addition of suitable surface active agents(emulsifiers) including mono or diglycerides and/or lecithin.
- Salt and other additives such as anti-oxidants, vitamins, color, flavor, etc. are included.
- Margarine processing involves basically premixing of ingredients followed by rapid chilling (solidification) and homogenization.

MARGARINE PRODUCTION

Nbd* oils

↓

Hydrogenation

↓

Mixing the oils and fats for fat phase.
Oil soluble additives(β-carotene, vit A, D, emulsifiers lecithin, MDG)

Milk phase
milk
starter culture
(*Streptococcus lactis*
Streptococcus cremoris-
producing aroma)
NaCl
Preservatives

↓

Emulsification

↓

*NBD: Neutralised,bleached, deodorised)

MARGARINE PRODUCTION

↓

Emulsification

↓

Cooling + crystallization (votator)

↓

Kneading

↓

Packaging

Product texture is homogenized through repeated crystallizations

Polymorphism

- Polymorphic forms are solid phases of the same chemical composition that differ in crystalline structure, but yield identical liquid phases upon melting.

Crystal Stability:

- Monotropic - one stable crystal form and one meta stable form regardless of temperature change

- One single “triglyceride” is “monotropic”, but fats are not: they contain many different triglycerides and therefore may possess “polymorphism”.

In formulating margarines, incorporation of air, plasticity, consistency and solid-liquid ratio are important characteristics that depend, in part, on this polymorphism (i.e. α, β and β' types of crystal formation).

Polymorphic Forms

How they are formed:

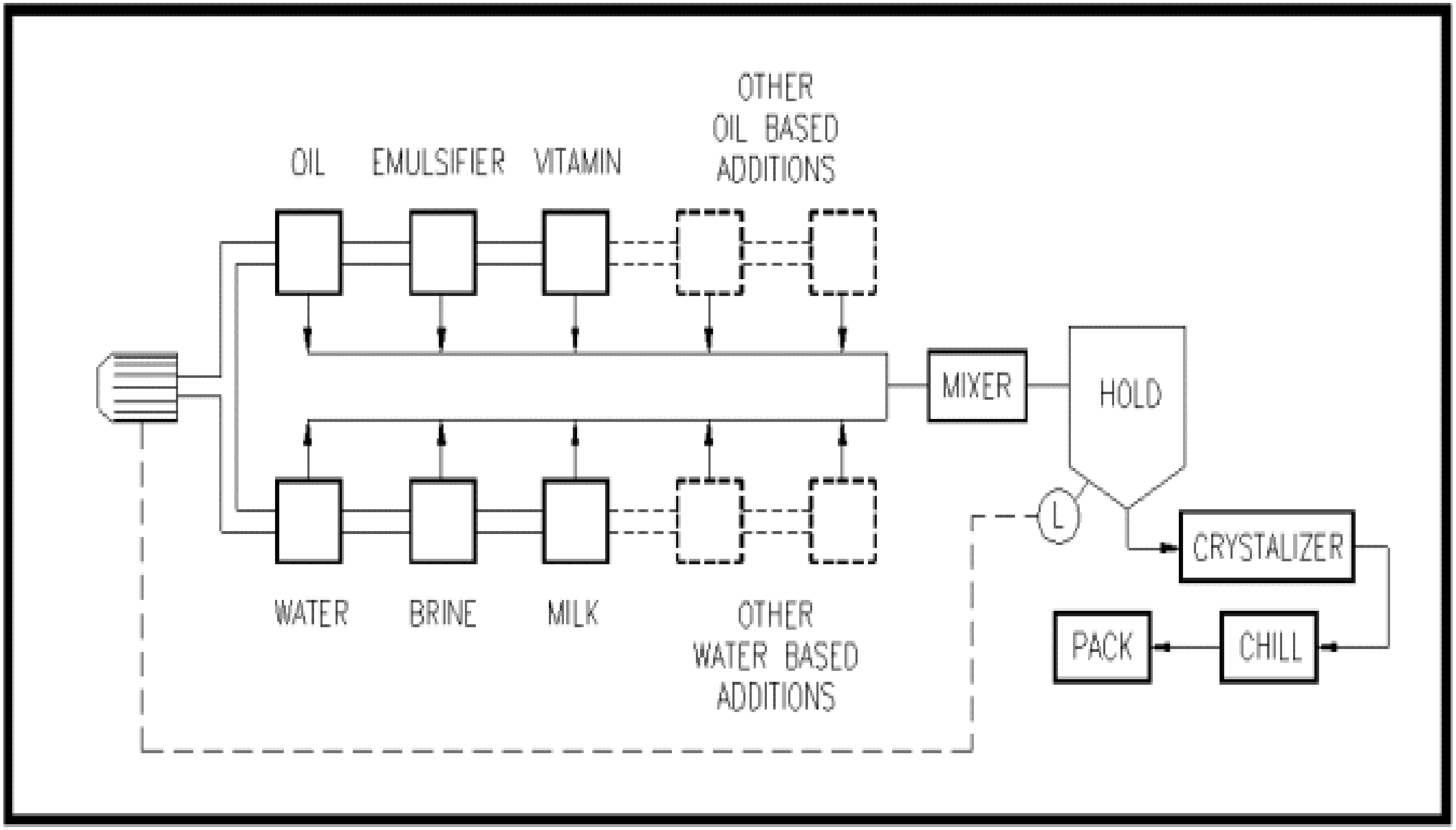
- α form of crystals form upon cooling from the hydrogenated melt: lowest M.P. Density Least (crystal size: 5μ), Translucent
- Upon further cooling, β form of crystals form: Highest M.P., High Density (crystal size: 25-50μ) Opaque
- Heating back α to its melting temperature yields β' form of crystals: medium M.P., medium Density , (crystal size: 1μ) Intermediate

Polymorphic Forms

- β' Crystals - large amounts of small air cells- Yields whiter, creamier product that is tender and has a smooth texture

- β Crystals - small amounts of large air cells - Yields large clustered crystals with a waxy or grainy texture

- So , β' Crystal forms are preferred in margarines since they incorporate more air.

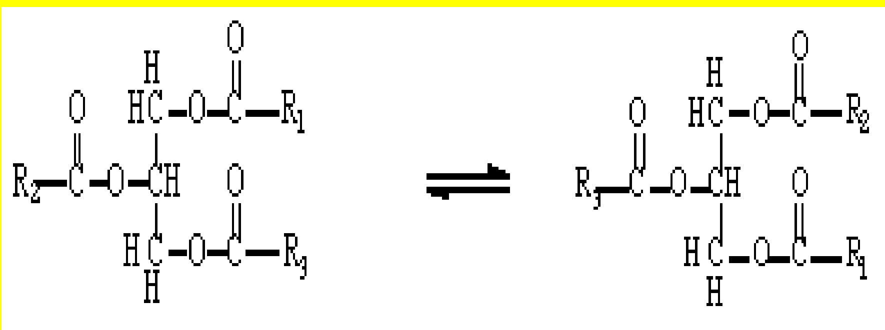

OTHER
OIL BASED
ADDITIONS
OIL
EMULSIFIER
VITAMIN
MIXER
HOLD
L
CRYSTALIZER
CHILL
PACK
WATER
BRINE
MILK
OTHER
WATER BASED
ADDITIONS

Interesterification

- ***Definition: A basic treatment for the preparation of tailor-made fat specialties to change the physical properties of the oils and fats by statistically redistributing the fatty acids in the respective three available positions of the triglycerides(interchange of fatty acids between and inside the different triglycerides) without altering the fatty acid composition of the original oils and fats***
- **This process rearranges the fatty acids on the triglyceride backbone with a catalyst or enzyme to change the fat's properties. The lower cost and broad functionalities produced with hydrogenation made this method less desirable, but since it doesn't create trans isomers, commercial interest in interesterification has increased significantly**
- **Options: Animal or vegetable? Solid or plastic or liquid? Steep or broad melting curve? To *trans* or not to *trans*?**

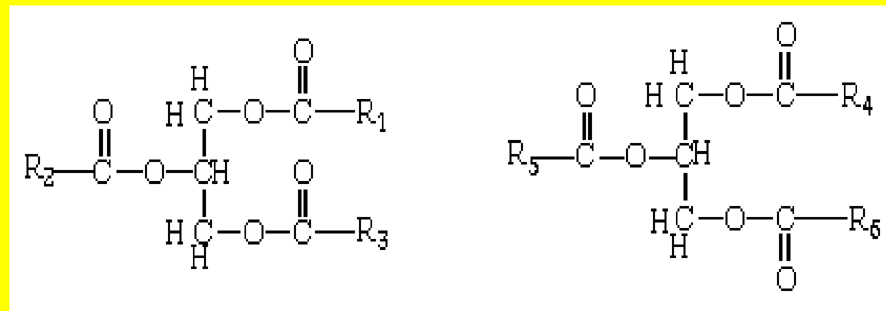
Interesterification within a triglyceride Or between triglycerides

Within a triglyceride:

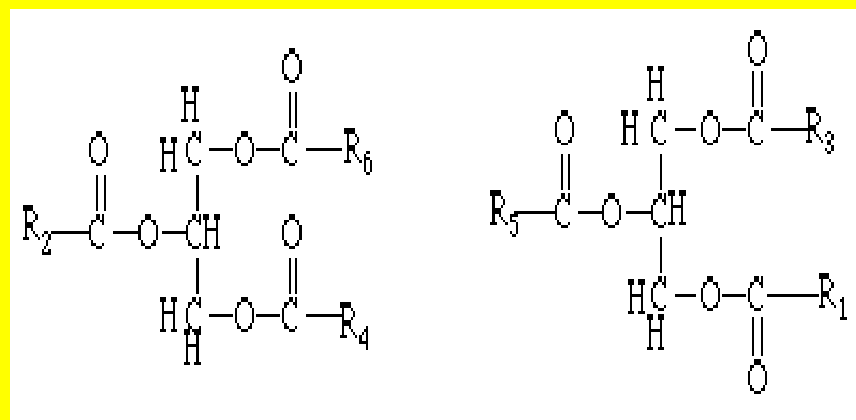


Between 2 triglycerides:

Start with:



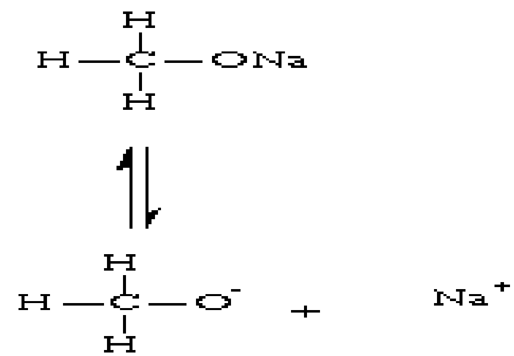
End with:



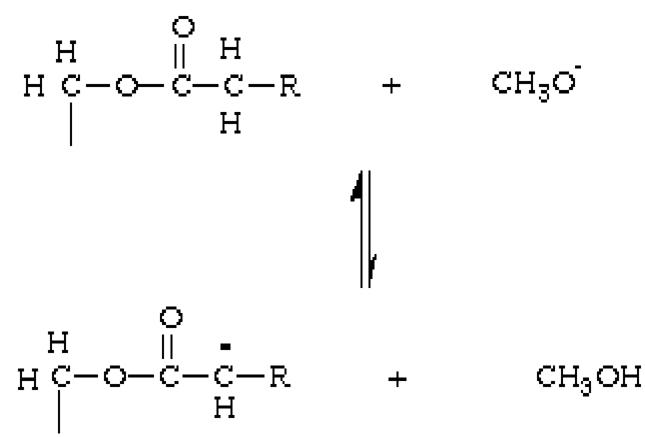
Chemical and Enzymatic Interesterifications

- Exchange of fatty acids may occur at 250 ° C with no catalyst or at 0° C with the proper catalyst.

The chemical catalyst used is usually "sodium methoxide"



İnitial Reaction:



Enzymatic Interesterifications

- By utilizing enzymes in place of chemicals, the oils are subjected to even less severe processing conditions.
- Enzyme interesterifications are more economical, increases processing flexibility, friendly for the environment, and also provides numerous desirable functional characteristics

Designer Fats for Bakery

- Fats provide a number of functions in baked goods. One of the most common is to “shorten,” or tenderize, texture (“shortening”).
- In addition to its texturizing effects, fat also contributes “moistness” or lubricity, which can help extend product shelf life, and influences flavor, either through its own contribution or by modifying or enhancing other ingredients’ flavor. It also modifies surface appearance; serves as the base for many bakery fillings, coatings and icings; and works as the heat-transfer medium in fried items, such as donuts and fried pies

TREND: “fine-tuning a product to fit to a specific customer’s line”

- Coating fats can be produced from coconut, palm-kernel and palm oils, as well as cocoa butter.
- Spray oils can be produced from coconut oil or “trait-enhanced” GM oils, such as high-oleic canola.
- Frying fats can be produced from tallow, palm and trait-enhanced oils.
- All-purpose shortenings can be produced from palm oil, or interesterified blends of fully hydrogenated soybean or cottonseed oils with trait-enhanced oils. In addition, emulsifier packages can be added to the foregoing to produce cake and icing shortenings. Tallow and lard are options as well.

Fat’s functionality: Structured Fats

- Example: Alpha-linolenic acid falls under the omega-3 fatty acid category and can be found in flaxseed oil (51% linolenic acid), canola oil (9%), soy oil (7%) and walnuts (7%). The body converts it to longer-chain (LC) omega-3 poly unsaturated fatty acids (PUFAs) eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) for use, although these can be consumed directly by using marine oils, particularly those from coldwater fish.

- Eating LongChain- PUFAs may reduce the incidence of coronary heart disease and stroke, and also aid brain and retina development and function. Several companies have developed processes that can produce omega-3 fatty acids from flaxseeds without a “fishy” taste. While product designers have to watch for potential oxidation problems from these unsaturated fats, they can act as nutritional enhancements in baked goods when added to the fat phase (or dry, beadlet forms also can be mixed in the flour).

Fractionation

At ambient or low temperature, some oils (or fats) are in the form of a mixture of a crystallised high melting point fraction and of a liquid low melting point fraction.

- **The purpose of fractionation process is to physically separate the liquid fraction called «oleins» from the crystallised fraction called «stearins». Fractionation is practised mainly on palm oil, palm kernel oil, lard, tallow, partially hydrogenated fish or soyabean oil and anhydrous milk fat.**
- **The process comprises three steps:**

  1. Conditioning, which consists in heating and homogenising the oil in maturators.

  2. Formation of crystals through selective crystallisation. The operation is conducted in several cooling steps.

  3. Filtration, for the separation of the oleins from the stearins.

Main Applications of Fractionation:
Salad dressing and frying oils (oleins), margarines, shortenings, confectionery (cocoa butter), pastry, bakery products and speciality fats

Cocoa Butter Alternatives
(Equivalents, Substitutes and Replacers)

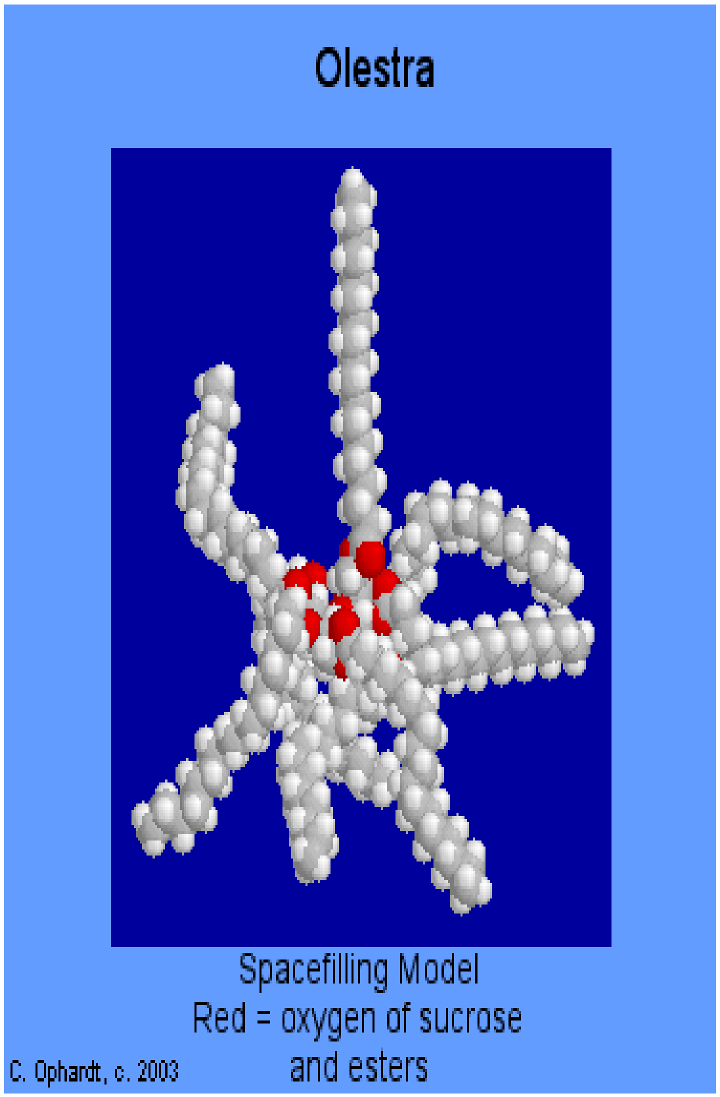
- A solvent-based fractionation is used for producing fats with melting properties similar to cocoa butter and compatible with it (in 1950's).
- Palm or palm kernel oil is fractionated into three fractions:

  *The top fraction contains only the trisaturated triglycerides ;

  *The bottom fraction contains di- and tri- unsaturated triglycerides;

  *The mid-fraction is a steeply-melting fat with excellent mouth-feel, like cocoa butter

OLESTRA



Olestra is a "fat substitute" that has the properties of a fat in flavor and texture, but is indigestible by enzymes which hydrolyse sucrose or the triglycerides. It does not add any calories as a normal fat would.Olestra is part fatty acids from cottonseed or soybean oils and part sucrose rather than glycerol in triglycerides. The six to eight fatty acids are bonded to the hydroxyl or alcohol groups on the sucrose using an ester synthesis reaction. This makes for a rather large molecule that looks like an octopus with many arms. Since the enzymes can not break down the olestra, it travels through the intestines undigested and unabsorbed.

In 1996, the FDA approved the use of olestra in potato chips, crackers and fried snacks, as it is the only heat stable fat substitute for fried foods. There have been some reports of adverse reactions in the intestines including diarrhea and cramps, indicating that it may act as a laxative in some people.

Since olestra is such a large nonpolar molecule, it may dissolve or combine with some of the fat soluble vitamins such as A, D, E, and K, and carotenoids. As a result, the FDA now these vitamins must be added to any products containing olestra.

FRYING

- **Mass Transfer**

  Water in a frying food migrates from the center to the surface. As water is removed at the surface due to heating, water is 'pumped' to the surface. The rate of water loss and its ease of migration through the product are important to the final characteristics of the food.

- **Heat Transfer**

  Water evaporation from the surface of a frying food also removes heat from the surface and inhibits charring or burning at the surface. The heat of vaporization of water to steam removes much of the heat at the food/oil surface.

  Heat Removal :As long as water is being removed at a sufficient rate, the surface of the food will not char. Subsurface water in the food will also conduct heat away from the surface and towards the center of the product.

  Interior Cooking :The transfer of heat to the interior of the product by water will result in cooking of the interior of the food. We want enough heat to 'cook' the product, but not enough to cause damage - example -French fry

FRYING OILS

The properties of oil change with frying. New oil has a high heat capacity that diminishes with use. Other factors such as viscosity may change dramatically with use.

- **Fresh Oil**
  Slight browning at edges of fry; partially cooked (gelatinization) centers; crisping of the surface; slightly more oil absorption.

- **Optimum Oil**
  Golden brown color; crisp, rigid surface; delicious potato and oil odors; fully cooked centers (rigid, ringing gel); optimal oil absorption.

- **Degrading Oil**
  Darkened and/or spotty surfaces; excess oil pickup; product moving towards limpness; case hardened surfaces

- **Runaway Oil**
  Dark, case hardened surfaces; excessively oily product; surfaces collapsing inward; centers not fully cooked; off-odor and flavors (burned).

ANIMAL FATS

1. **Milk fat(butter): It is obtained first by "churning" process, a mechanical process involving heavy mixing at cool temperatures and results in separation of a yellowish watery emulsion the continuous phase of which is lipidic. This emulsion, butter, contains ~ 20% water and exhibits plastic behavior at room temperature.**

   Butteroil is a dairy product which is created by removing the moisture and the nonfat milk solids contained in butter. It is obtained by mildly heating butter to liquify and allowing gravity separation(or fractionation) of the oil phase. It is much more stable than the butter emulsion.

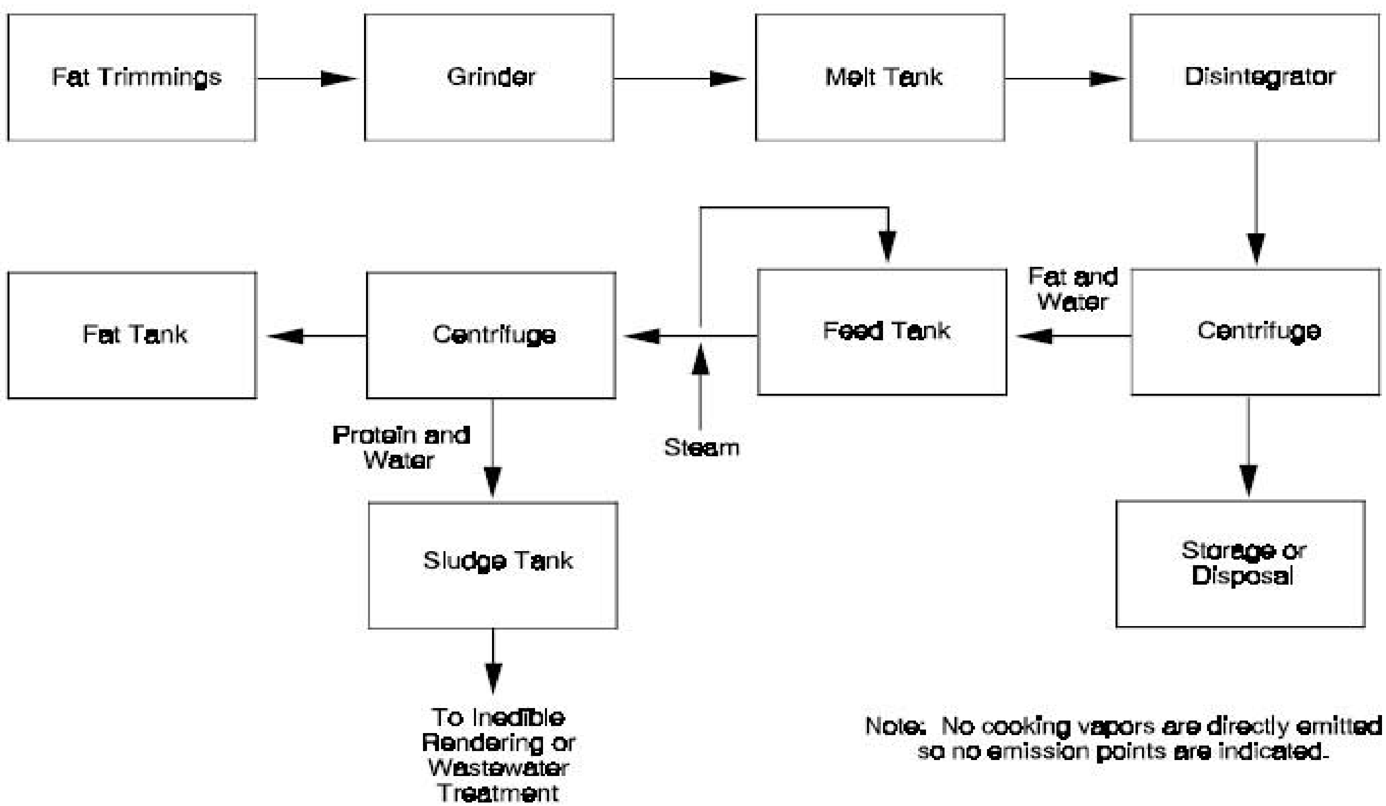
2. **Body fats of domestic farm(land) animals(cattle or sheep):**

Ex: Tallow and lard: composition is affected with animal type, age, and feed(grass-fed :harder tallow; grain-fed:softer). Slaughterhouse refuse is heat-treated in cookers and separated by gravity from non-fat parts.

The "rendering" process" involves the crushing and heating of the raw material supplied from slaughterhouses, leading to the evaporation of the moisture in the material, which then enables the fat, known as 'tallow', to be separated from the remaining high-protein solids, known as 'greaves'*.

***The greaves are further processed by pressing, centrifuging or by solvent extraction in order to remove more tallow. The resultant protein-rich material is then ground into meat and bone meal.**

RENDERING



Fat Trimmings
Grinder
Melt Tank
Disintegrator
Centrifuge
Fat and Water
Feed Tank
Steam
Centrifuge
Fat Tank
Protein and Water
Sludge Tank
To Inedible Rendering or Wastewater Treatment
Storage or Disposal
Note: No cooking vapors are directly emitted so no emission points are indicated.

Fish Oils

Fishmeal and fish oil are produced by a continuous and carefully controlled process which involves cooking, pressing, drying and milling of fresh, raw fish. Yields of fishmeal and fish oil can vary between fish species and even from season to season, but typically around 17 – 22% fishmeal and 5 –15% fish oil will be obtained by processing.

Production Process:

- **1. Intake – Raw fish is sampled and analysed on intake to check for freshness and expected yield of meal and oil.**
  2. Cooking - The raw fish is conveyed through a steam heated continuous cooker, where it is heated to 90°C-95°C. This sterilizes the fish, coagulates the proteins and disrupts the cell membranes to facilitate the separation of the solubles and the oil from the dry matter.
- **3. Press - The cooked raw material is fed to a screw press where much of the liquid is squeezed out to form a presscake which is conveyed to the drier.**
- **4. Separator – The press liquid contains water and most of the oil from the fish, as well as dissolved proteins, salts and fine particles. These particles, sometimes called sludge, are removed in a decanter and transported to the drier to be mixed in with the presscake. The liquid from the decanter is fed to separators where the oil is removed and can subsequently be stored in large tanks for export.**
- **5. Evaporator - The water phase from the separators is fed to the evaporators where it is gently concentrated before being blended with the presscake during the drying stage.**
- **6. Drier - The water in the press cake, sludge and concentrate is removed by rapid air drying after which the fishmeal is cooled, milled and stored for export.**

Fish Oil Production