Lipids

FOOD CHEMISTRY–OENOLOGY I

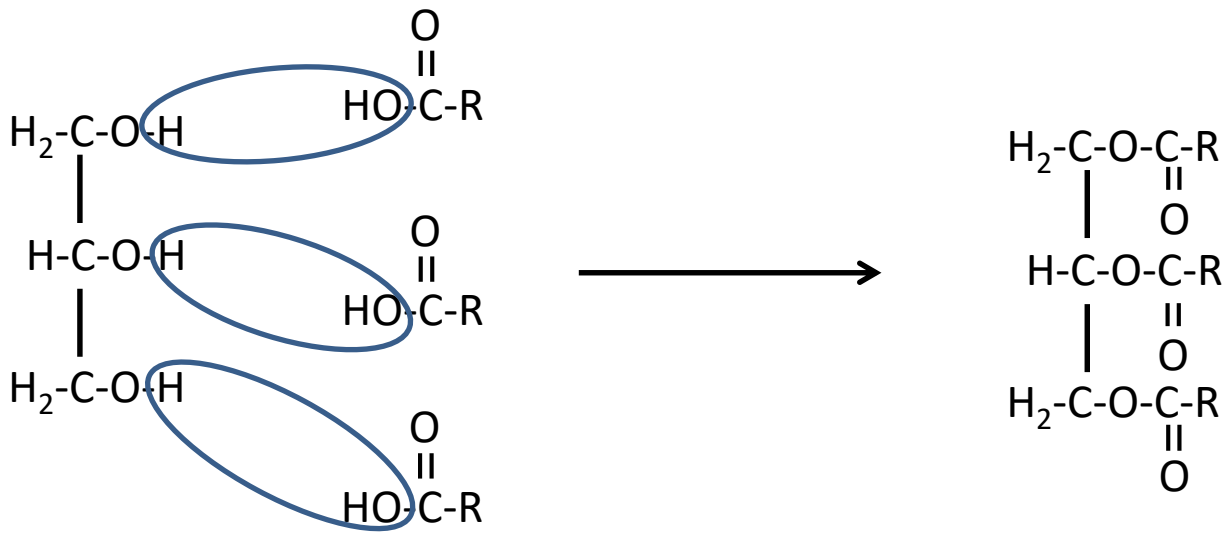
Lipids

- Lipids are a family of compounds that are extracted from biological substances with **non polar solvents**, such as ether, benzene, chloroform, petroleum ether, etc.
- Lipids include:
  - Fatty acids and their glycerides
  - Phosphatides (glycerol phosphate and sphingosine derivatives)
  - Glycolipids (glycerol and sphingosine derivatives)
  - Waxes
  - Isoprene derivatives (terpenes, steroids)

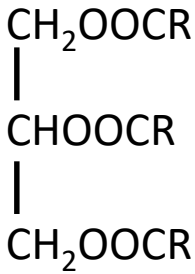
Fats and oils

Composed of:

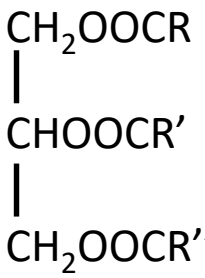
- Mainly glycerides
- In smaller percentages:
  - Higher fatty acids
  - Sterols
  - Vitamins
  - Phosphatides
  - Pigments
  - Waxes
  - Odorous substances



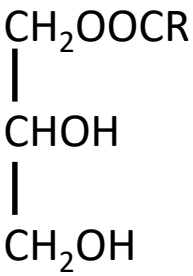
Glycerol **Organic fatty acid** **Triglyceride**



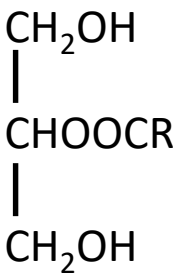
Simple triglycerides



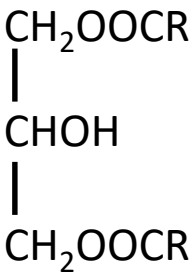
Mixed Triglycerides



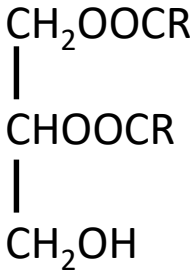
A-type triglycerides



B-type triglycerides



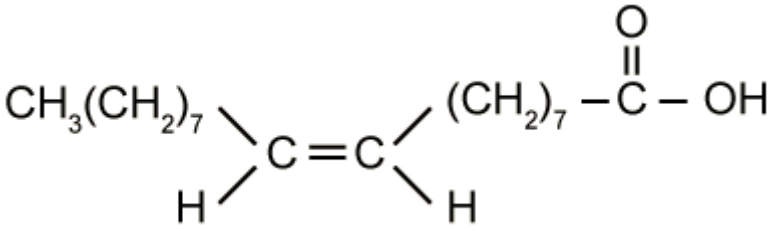
A,A-type triglycerides



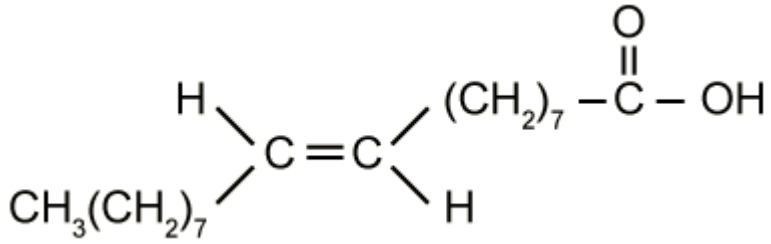
A,B-type triglycerides

Saturated fatty acids

Palmitic	$C_{15}H_{31}COOH$	(component of fats and oils)
Stearic	$C_{17}H_{35}COOH$	(component of fats and oils)
Butyric	$CH_3CH_2CH_2COOH$	(component of butter)
Caproic	$C_5H_{11}COOH$	(found in goat butter)
Capric	$C_9H_{19}COOH$	(component of butter)
Caprylic	$C_7H_{15}COOH$	(component of butter, coconut oil)
Lauric	$C_{11}H_{23}COOH$	(component of laurel oil)
Myristic	$C_{13}H_{27}COOH$	(found in many lipids)
Arahidic	$C_{19}H_{39}COOH$	(found in peanut oil)



Oleic acid



Elaidic acid

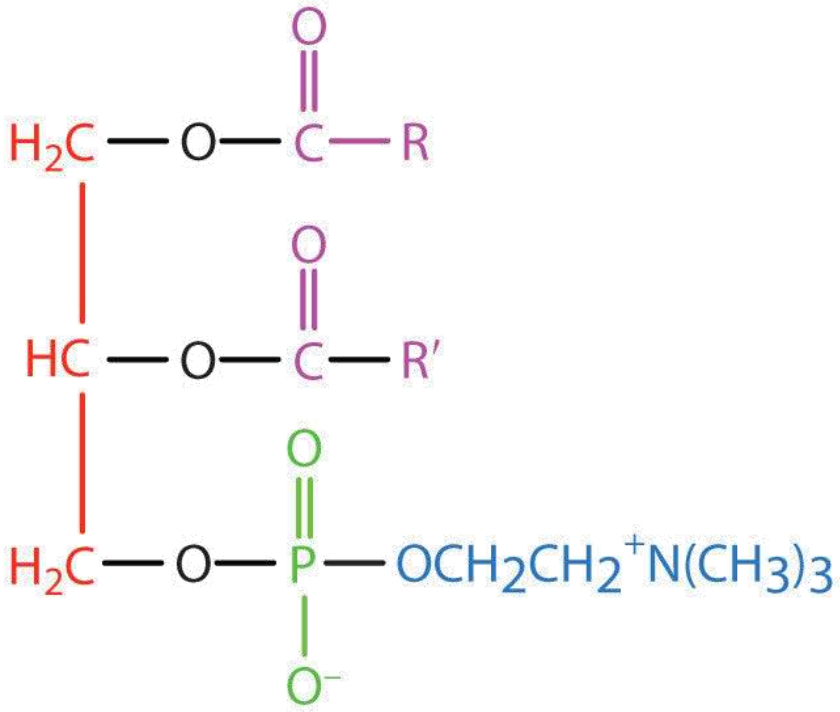
Unsaturated fatty acids

Oleic	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Elaidic	Trans isomer of oleic acid
Palmitoleic	$C_{16}H_{30}O_2$ 9-hexadecenoic
Linolenic	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$ (component of linseed oil)
Linoleic	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$ (component of linseed oil)
Eleostearic	$CH_3(CH_2)_3CH=CHCH=CHCH=CH(CH_2)_7COOH$

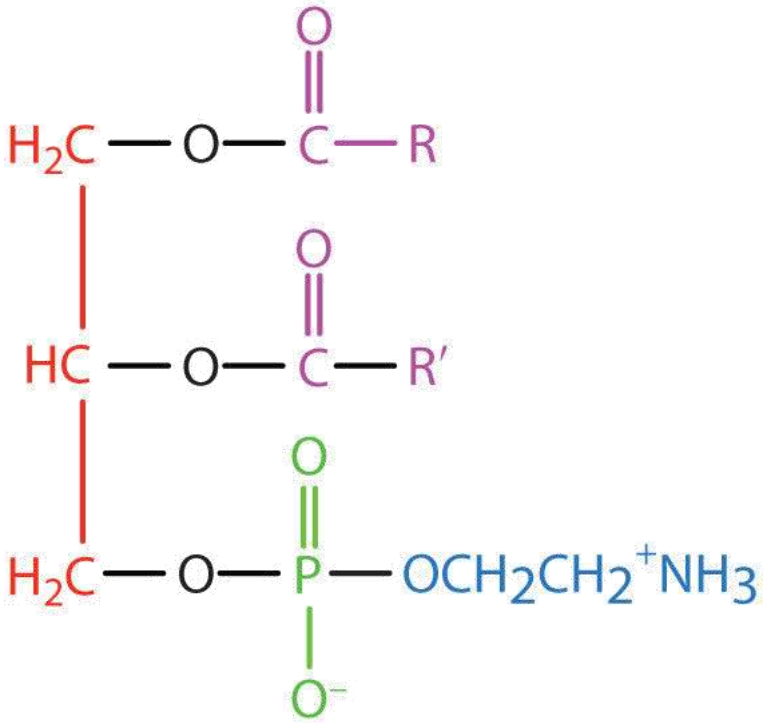
Other unsaturated fatty acids found in fatty substances:

Caprylic	$C_{10}H_{18}O_2$ 9-dodecanoid acid
Lauric	$C_{12}H_{22}O_2$ 9-dodecanoic acid
Arahidonic	$C_{20}H_{32}O_2$

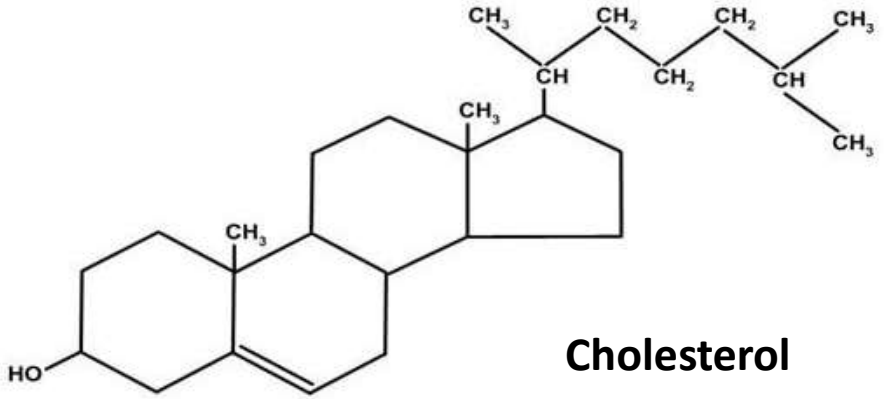
Phospholipids



Lecithin

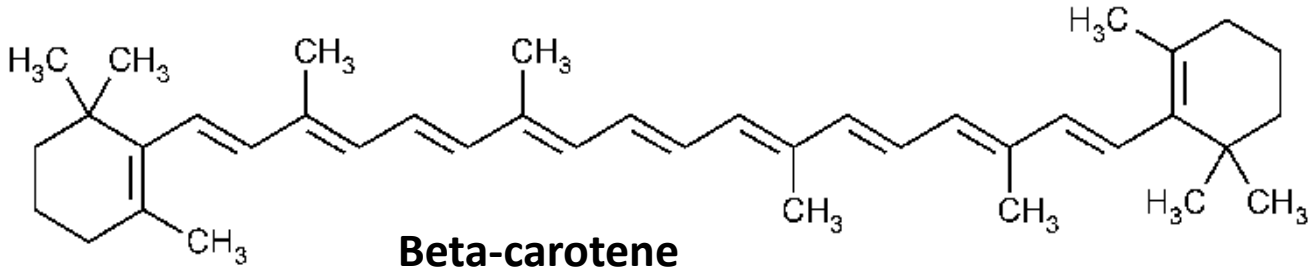


Cephalin

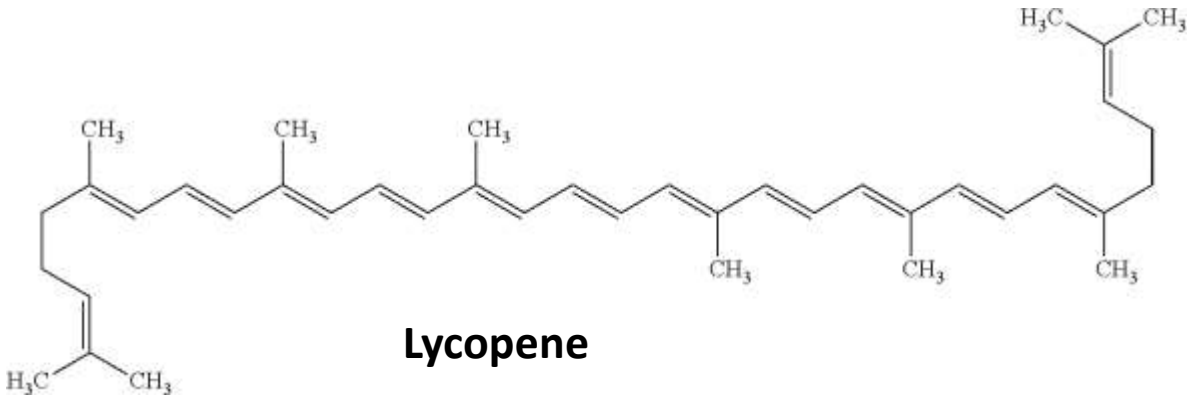


Cholesterol

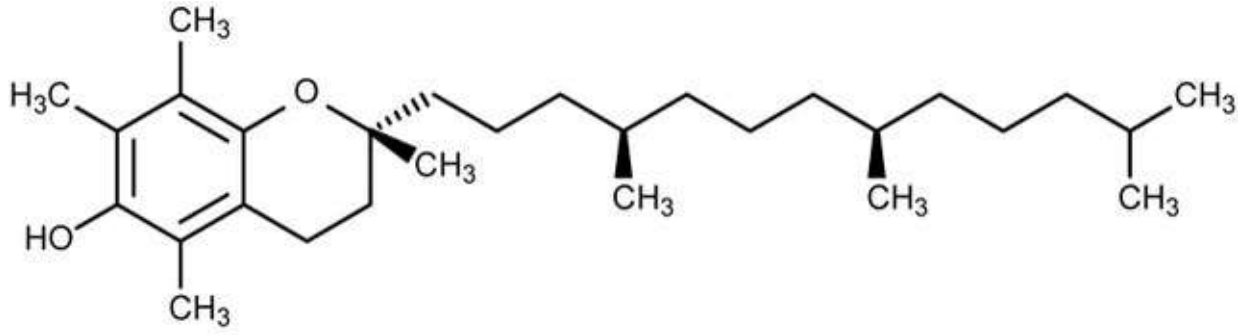
Fatty acids also consist of pigments. This category involves carotenoids, chlorophylls, anthocyanins and the unsaturated hydrocarbon lycopene.



Beta-carotene



Lycopene

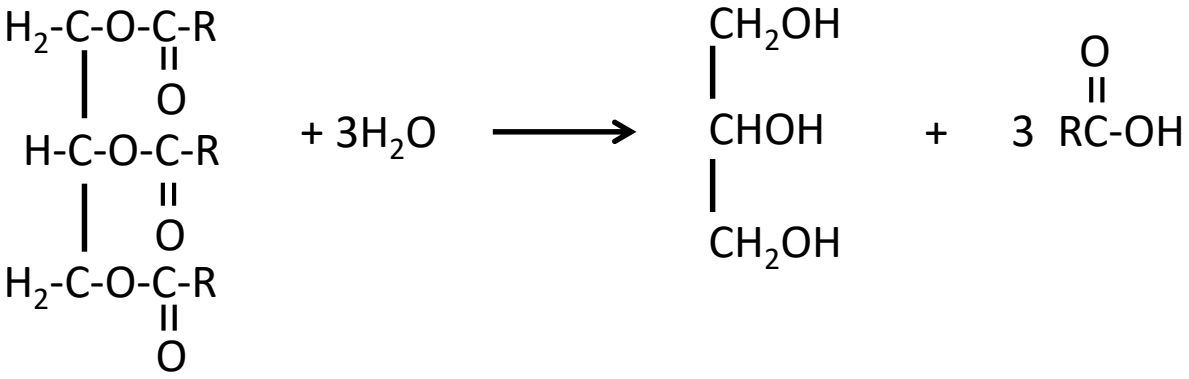


Tocopherol

Chemical reactions of lipids

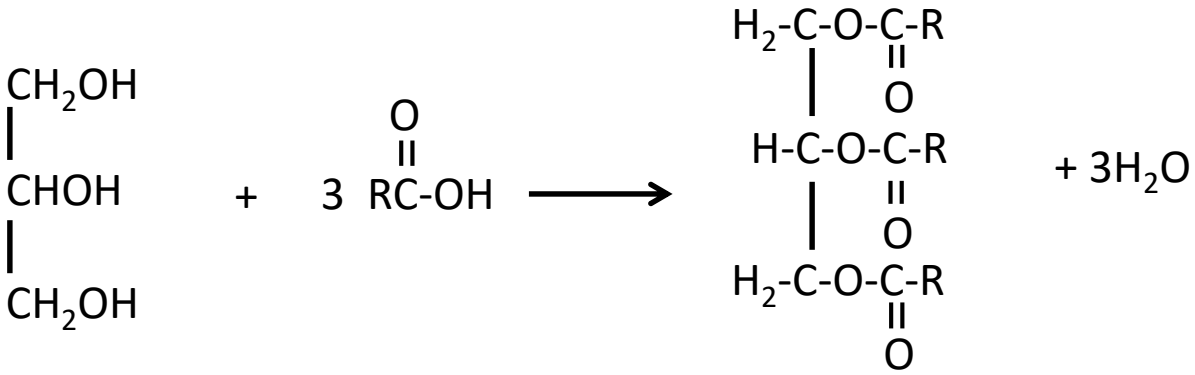
Hydrolysis, acid esterification, alcoholysis, saponification, halogenation, hydrogenation

1. Hydrolysis



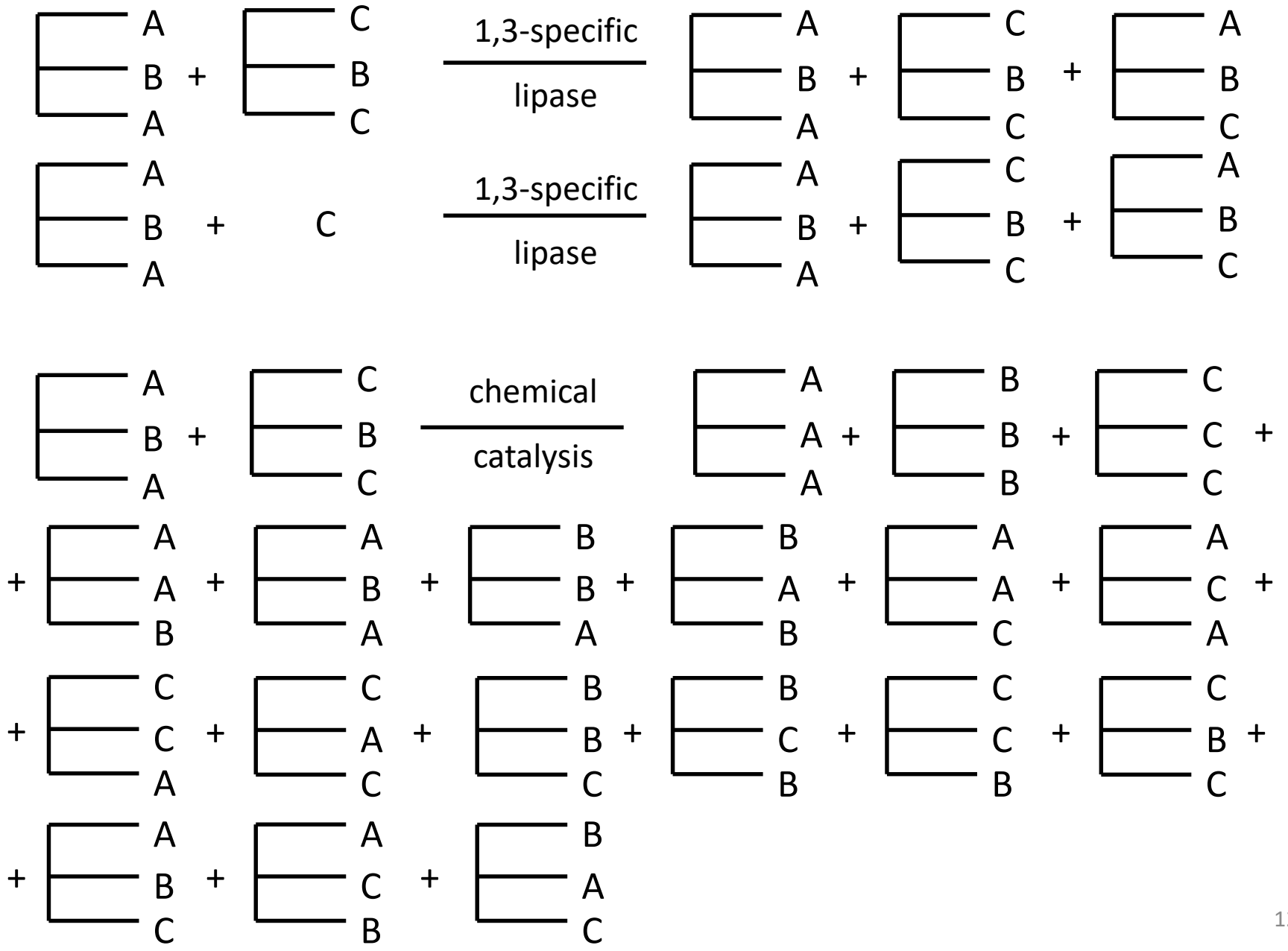
Catalyzed by: acids, alkalis, lipolytic enzymes

2. Esterification

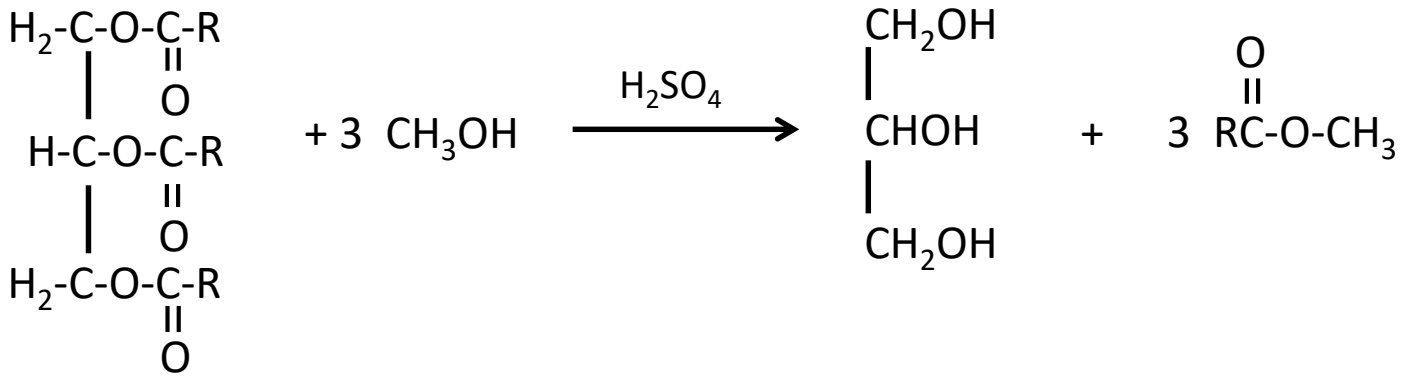


Catalyzed by acids and alkalis

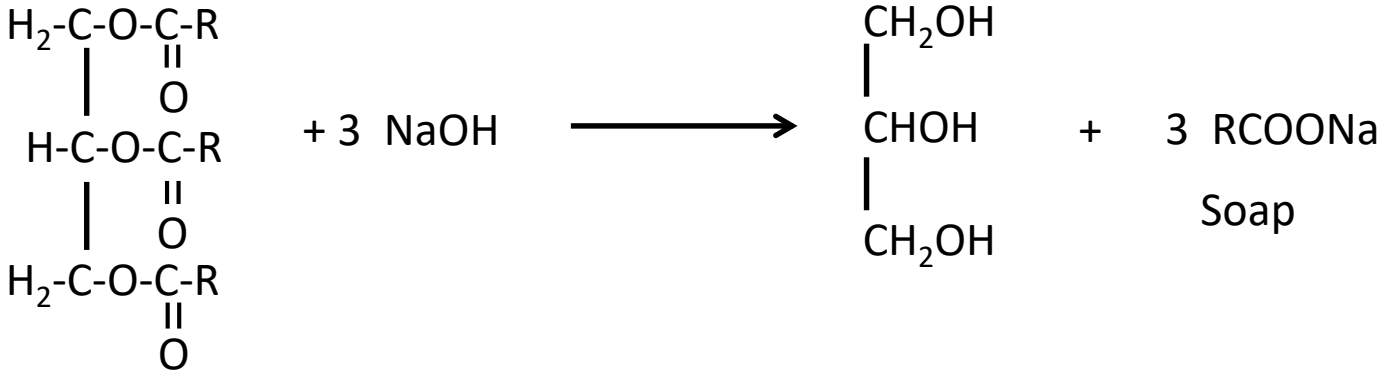
Enzymic esterification using 1,3-specific lipase



3. Alcoholysis



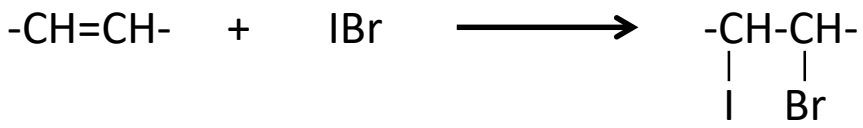
4. Saponification



Saponification number

5. Iodine Number

Iodine values or iodine numbers are the g of iodine that are bound by 100 g of a lipid substance.

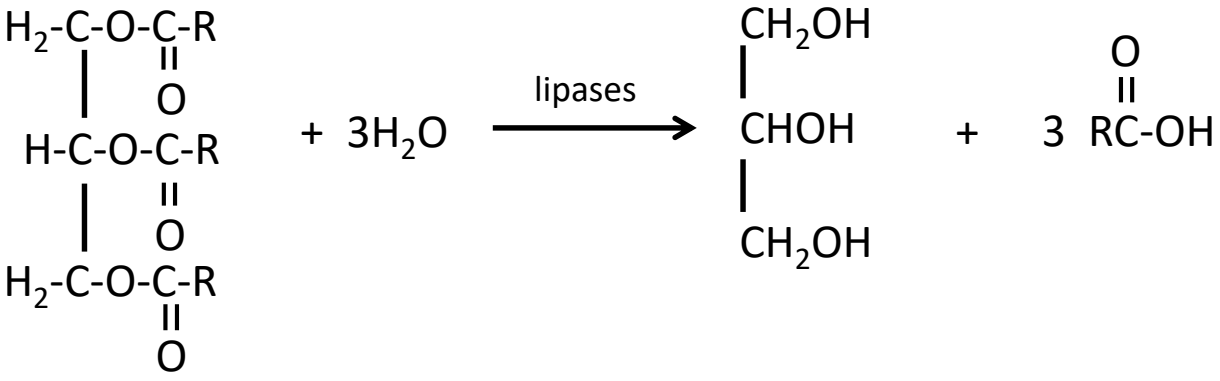


Spoilage of lipids and oils

1) Hydrolysis of fatty acids
2) Oxidation of fatty acids

1) <u>Fatty acid Hydrolysis</u>

Into glycerol and free fatty acids



2) <u>Oxidation of fatty acids</u> ⟶ Odorous substances

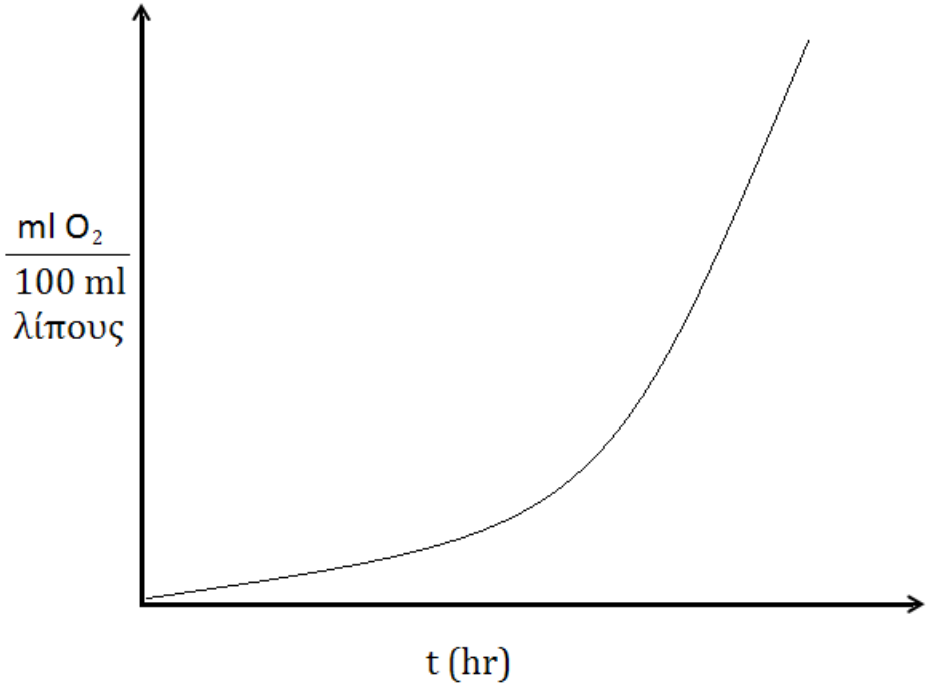
2a) Due to the enzyme Lipoxidase

2b) Duo to atmospheric Oxygen (autoxidation). Steps:

- Initiation (short term O_2 intake)
- Propagation (rapid O_2 intake)
- Termination (decreased O_2 intake)

Factors that affect the oxidation of fatty substances:

i. Concentration of fatty substances in unsaturated fatty acids
ii. Temperature
iii. Humidity
iv. Light
v. Presence of O_2
vi. Presence of substances that favor oxidation (pro-oxidants, Cu, Fe, etc.) or prevent it (antioxidants, etc.)



Rate of atmospheric oxygen absorption from fatty substances

The oxidation mechanism with free radical chained-reactions consists of three steps: α) Initiation, β) Propagation, γ) Termination

Initiation

$$R\text{-}H \xrightarrow[\text{cleavage}]{\text{Homolytic}} R^{\cdot} + H^{\cdot}$$

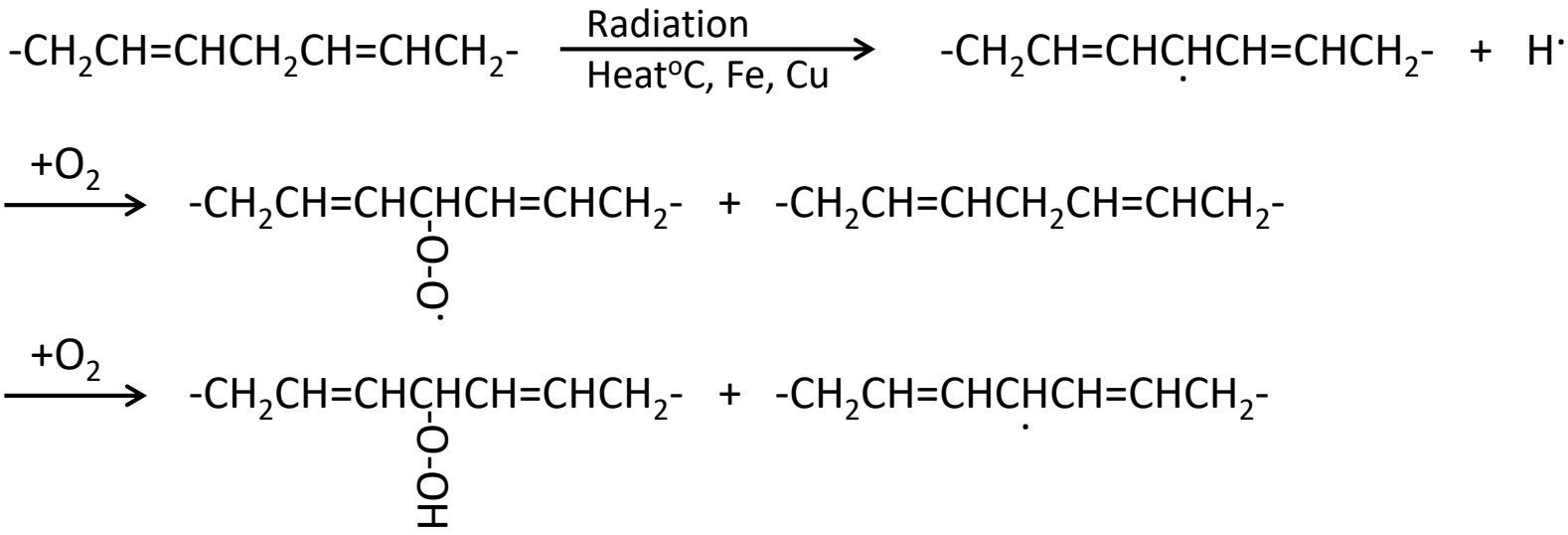
Propagation

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$$

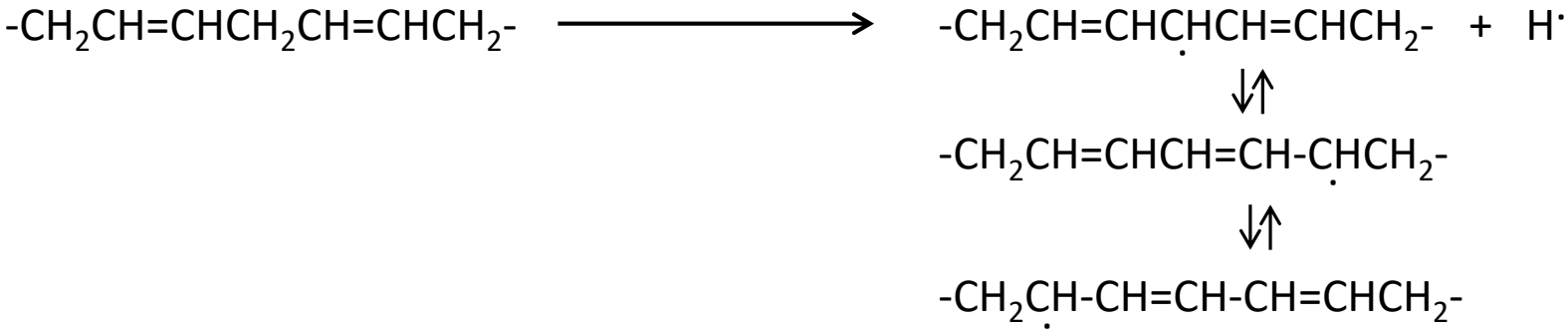
$$ROO^{\cdot} + RH \longrightarrow R^{\cdot} + ROOH$$

Autoxidation process:

Chain reactions and the formation of free radicals (valence electrons):

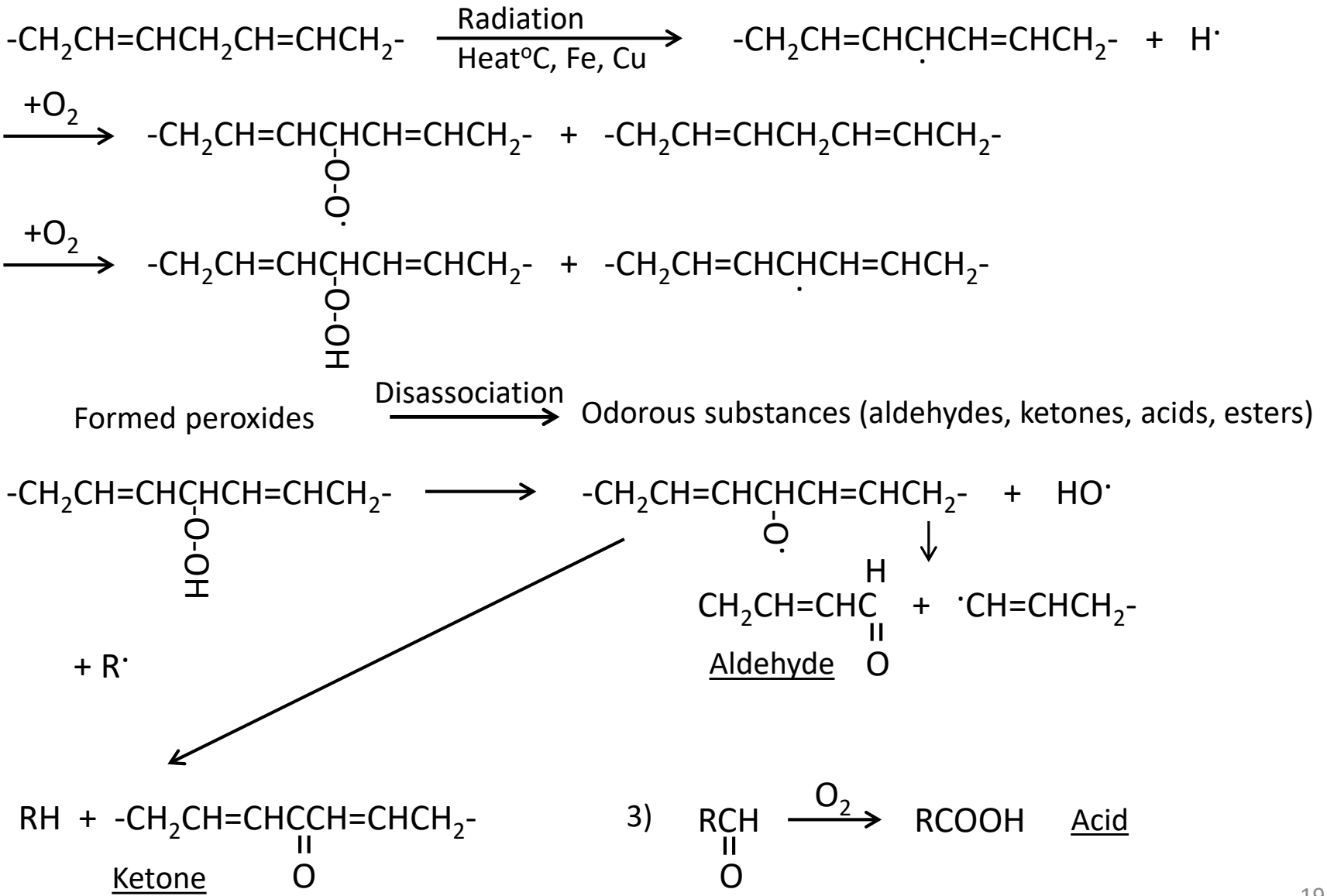


The more unsaturated the glycerides of the fatty matter, the more susceptible the fatty matter is to oxidative rancidity.



Autoxidation process:

Chain reactions and the formation of free radicals (single valence electrons):



Other lipidic matter oxidations:

Fatty Matter —(Ketonic rancidity, fungus)→ Different kinds of Ketones

Fatty Acids ——→ Methyl-ketones, Roquefort cheese, etc.

Various research results:

1. Fatty substances with more unsaturated acids oxidate faster.
2. Animal fats oxidize faster than plant fats due to secondary antioxidants (tocopherols).
3. Refined oils oxidize faster than unrefined oils, due to destruction of the primary natural antioxidants (tocopherols).
4. Free fatty acids deteriorate faster than glycerides.
5. Good quality oil mixing with oxidized oils causes deterioration.

Preventing the oxidization of fatty matter

With antioxidants:

Natural antioxidants: tocopherols, phenyl compounds
Synthetic antioxidants: phenyl compounds

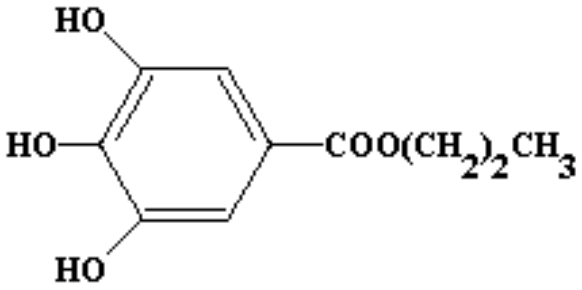
How antioxidants (AH) work:

They produce free radicals ·A, that bond R· groups

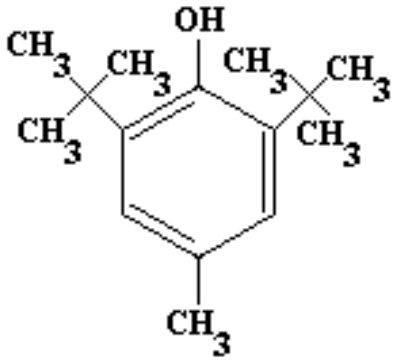
$$R\cdot + AH \longrightarrow RH + A\cdot$$

$$A\cdot + \cdot A \longrightarrow A\text{-}A$$

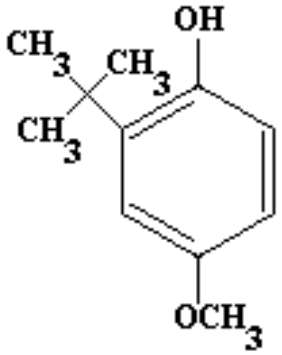
$$A\cdot + \cdot R \longrightarrow A\text{-}R$$



Gallic acid propyl ester (PG)

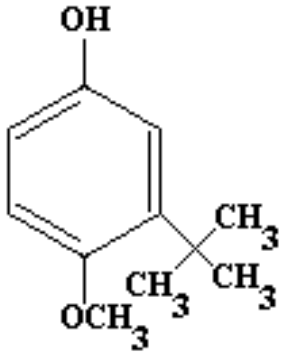


3,5-Di-tert-butyl-4-hydroxytoluene (BHT)



2-tert-butyl-hydroxyanisole

BHA



3-tert-butyl-hydroxyanisole

The maximum antioxidant doses that are approved from the Greek Government are:

PG	BHA	BHT
0,2%	0,2%	0,2%

Measurement of the oxidation of a fatty substance

Peroxide value

Equals to milliperoxide equivalents/kg fat = 1000 aN/b

a= consumed ml of $Na_2S_2O_3$
N= regularity $Na_2S_2O_3$
b= sample weight, g

$$ROOH + 2HI \longrightarrow R\text{-}OH + H_2O + I_2$$

peroxide

$$2Na_2S_2O_3 + I_2 \xrightarrow{\text{starch}} Na_2S_4O_6 + 2NaI$$

Measurement of the oxidation of a fatty substance using spectomentry

Linoleic acid: $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$

↓ Oxidation

Peroxidation of linoleic acid (absorption 232nm)

↓ oxidation

Secondary oxidation products α-diketones, unsaturated α-ketones (absorption 270nm)

Assessment of the stability of a fatty matter

1) Active oxygen method

Fat matter $\xrightarrow[O_2]{100^o\ C}$ Peroxides

Peroxide measurement

2) Foods containing fats and oils (biscuits, etc.)
Active oxygen method

Food in an oven with 63° C ⟶ Rancidity, time measurement

Inversion of odour in refined or hydrogenated or deodorized fats

Odorous products:
$CH_3(CH_2)_3CH=CHCHO$, 2-heptanel
OHCCH=CHCHO maleic aldehyde
CH_3CHO Acetaldehyde
$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3$ di-propylketone
$CH_3(CH_2)_4CH=CHCH=CHCHO$ 2,4 Decadierenal

It is hindered by citric, tartaric acid and sorbitol.

Refinement

Crude oils extracted from various raw materials often contain:
1. Cellular matter or derivatives
2. Free fatty acids and phosphatides
3. Pigments
4. Odorous compounds e.g. aldehydes, ketones, etc.

Step 1
Removal of cell debris by filtration or centrifugation
Step2
Removal of fatty free acids by steam distillation and then neutralization

Refining by vacuum steam distillation

When fatty matter has a lot of free fatty acids. This is followed by neutralization of the rest, and helps to deodorize fats.

Alkali neutralized refining

Used: NaOH (caustic soda) or
Na_2CO_3 (soda)

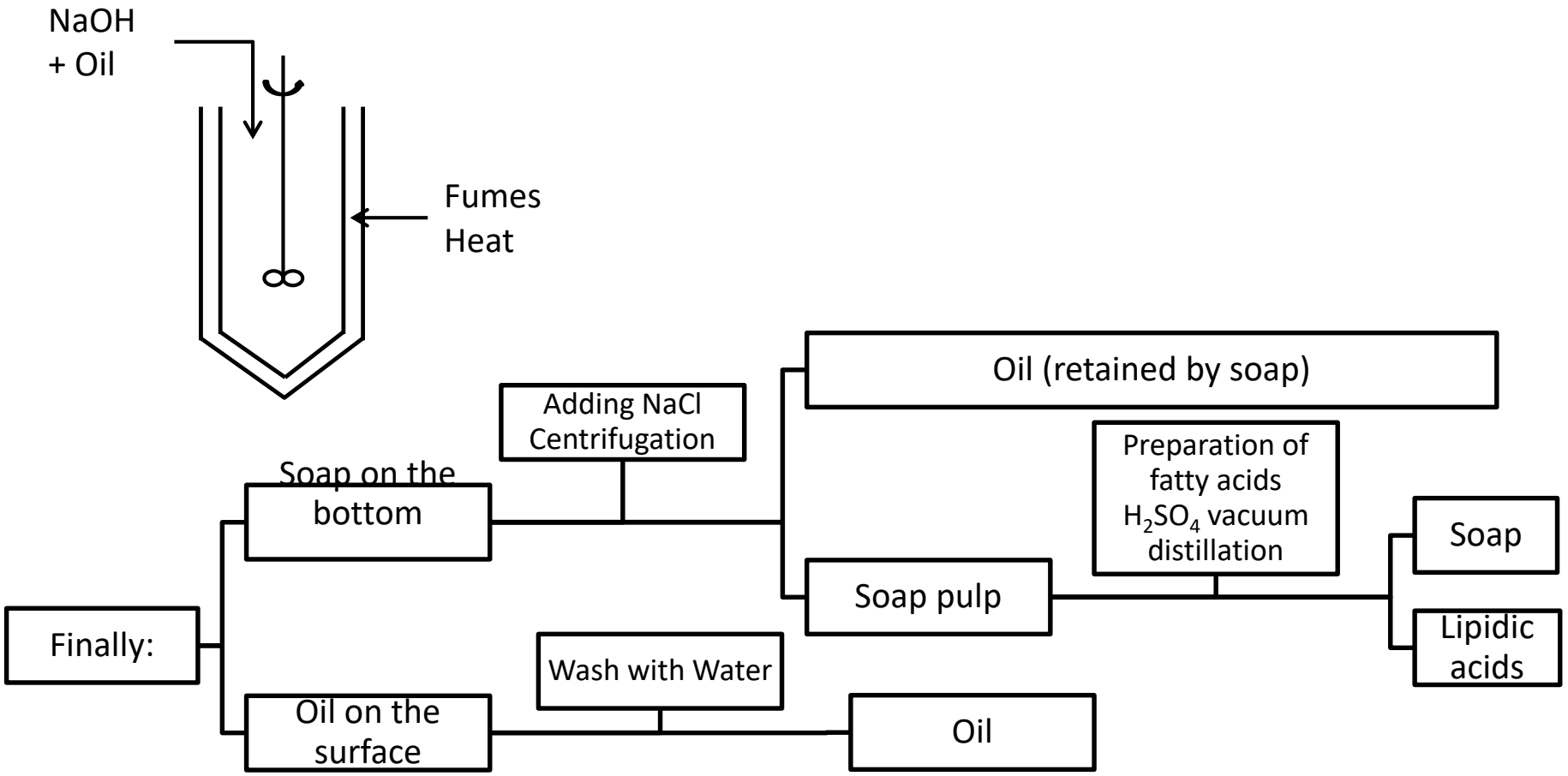
Discontinuous and continuous process

Industrial fatty technology includes:

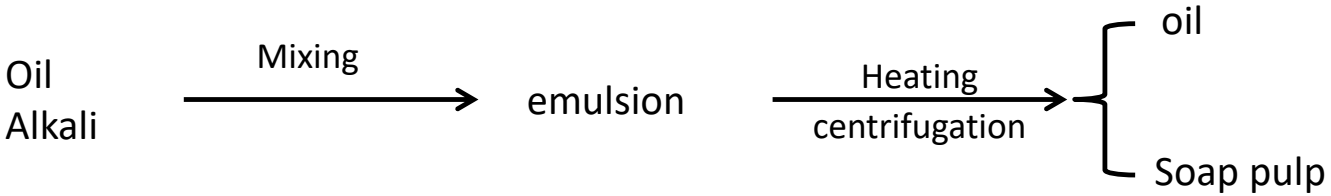
1. Processes for their recovery from animal or vegetable raw materials
2. Processes to improve their quality
    a. Refining
    b. Discoloration
    c. Deodorizing
    d. Hydrogenation

1a. Fat matter storage
1b. Collecting fats from raw materials
    i. By melting
    ii. By pressing (pressing, centrifugation)
    iii. By extraction (CS_2, CCl_4, $CHCl=CCl_2$, gasoline, acetone)

Discontinuous procedure



Συνεχής διαδικασία



Discoloration

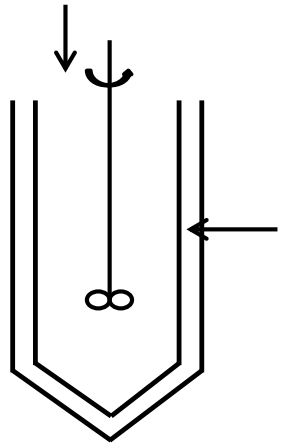
Pigment adsorbents:

- Activated carbon
- Diatomaceous earth

Equipment:
Discontinuous and continuous operation

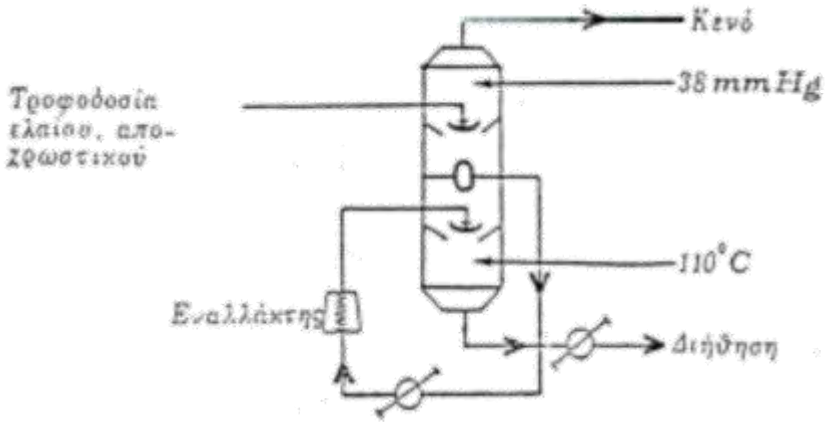
Discontinuous operation under vacuum

Dry fat (80°C)
Discoloring substance



Fumes
Heat (60-80°C)

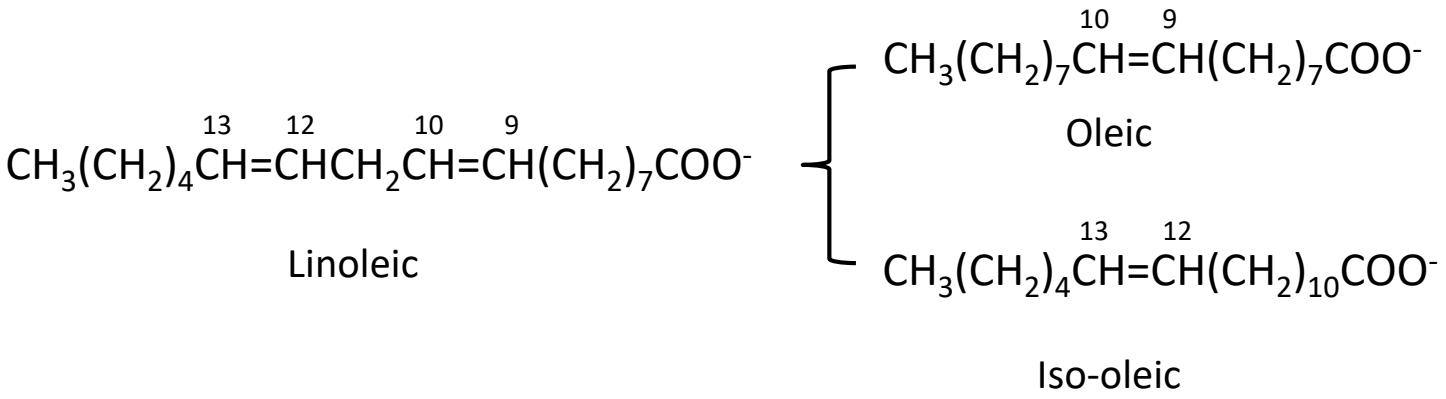
Continuous operation



Hydrogenation

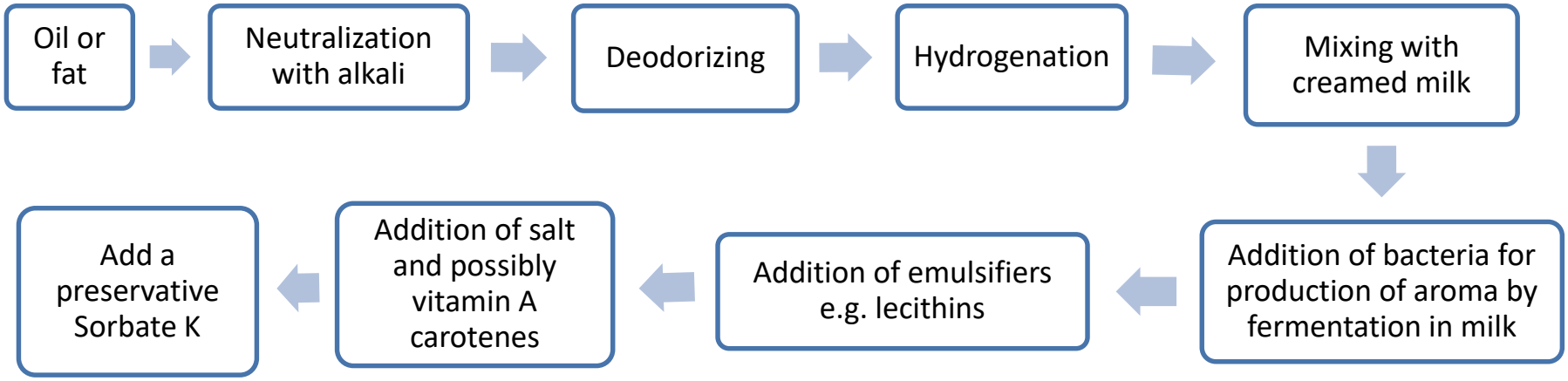
Adding hydrogen to double bonds of oils and lipids. Hydrogenation happens when warm oil mixes with a catalyst (powder) in a H_2 atmosphere and catalyst N:

For example:



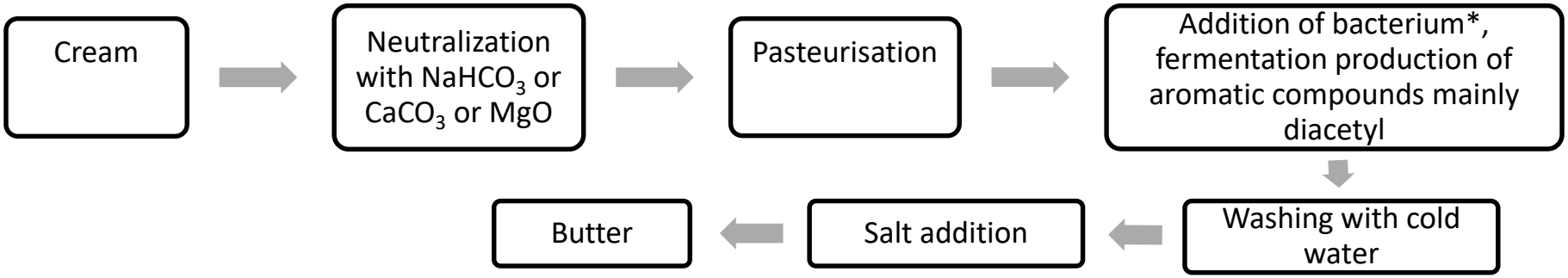
Liquid Oil ⟶ Solid fat
Plasticity

Margarine



Butter

At least 80% butterfat



*citric acid present in butter cream $\xrightarrow[\textit{Streptococcus citrovorus}\ \textit{Streptococcus paracitrovorus}]{\text{Bacteria}}$ Diacetyl $CH_3COCOCH$

*lactose present in butter cream $\xrightarrow[\textit{Streptococcus lactis}]{\text{Fermentation}}$ Lactic acid, acetic acid, propionic acid