Chem Factsheet

www.curriculum-press.co.uk Number 227

Fats and Oils

Introduction

Fats and oils are natural materials found in both animals and plants. They are particularly important for insulation against the cold, protecting body organs against physical shocks, promoting healthy cell functions while warding off disease and maintaining healthy hair and skin. They also act as vital energy stores which can be converted to glucose by the liver in times of need.

Some fatty acids (see later) are *essential* nutrients since they cannot be manufactured in the cells from other materials. Fats/oils containing these must be eaten to provide a healthy diet. However, all other fatty acids required by cells are *non-essential* and can be produced in the body from other compounds.

Fatty/oily foods are also essential since they provide vitamins A,D,E and K – the *fat soluble* vitamins!

General properties

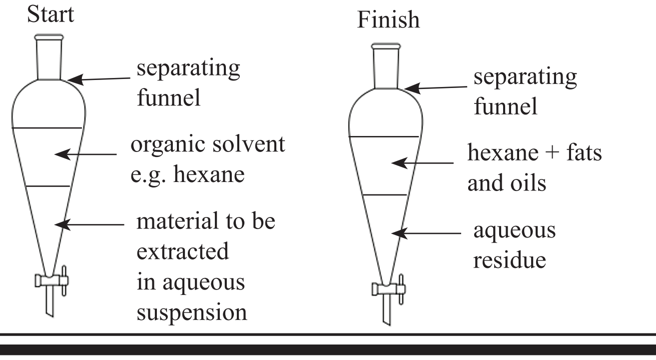
All fats and oils are very closely related in terms of chemical structure (see later) but the term "fat" is usually reserved for those which are *solid* at room temperature [e.g. lard, whale blubber etc.] while "oil" refers to those which are *liquid* at room temperature [e.g. fish oils, olive oil etc.]. Fats and oils are insoluble in water but soluble in organic solvents such as hexane (C_6H_{14}) or tetrachloromethane (CCl_4). Since they are water insoluble, they are found in "watery" foods such as milk in the form of an *emulsion* – tiny droplets of fat/oil suspended in water and prevented from coalescing by repulsive charges on the droplet surfaces.

Isolation and identification

The difference in solubility allows the extraction of fats and oils from tissues by a process known as *solvent extraction*. A small scale version of this is illustrated in figure 1 but it can be scaled up and made into a continuous process during industrial processes.

Fig. 1 Solvent Extraction of Fats and Oils

1. Material from which fat/oil is to be extracted is broken down in a blender and suspended in water.
2. Suspension is added to a separating funnel.
3. Hexane is added on top of the aqueous suspension.
4. The contents of the funnel are mixed thoroughly by inversion and shaking.
5. The layers are allowed to reform.
6. The lower aqueous layer is run off and discarded.
7. The upper organic layer is run off and water traces are removed by adding crystals of anhydrous $CaCl_2$.
8. The $CaCl_2$ is removed by filtration and the hexane is allowed to evaporate leaving the extracted fats and oils.



The mixture of fats and oils that has been extracted can be separated into its constituents by high pressure liquid chromatography (hplc) as summarized in figure 2.

Fig. 2 HPLC separation and identification of fats and oils

The fat/oil mixture is dissolved in a liquid mobile phase (e.g. methanol) and pushed through the column under pressure by a pump

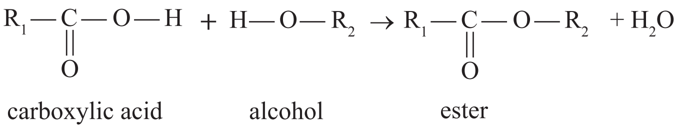
Separated components are collected or sent to a mass spectrometer sequentially for identification

1. The column is a thick, sealed metal (e.g. steel) tube able to withstand high pressure.
2. The stationary phase (SP) packed into this tube is a high boiling point liquid hydrocarbon held in the pores of an inert solid.
3. The mobile phase is liquid forced through tube by high pressure.
4. Fats/oils with a low affinity for the SP move through the column quickly whilst fats/oils with a high affinity move through slowly.

Chemical structure

Fats and oils are *esters*. In fact they are *tri-esters* but they are often referred to as *triglycerides*. An ester is a molecule containing a –COOC- group resulting from a *condensation* (also referred to as an *esterification*) reaction between a carboxylic acid and an alcohol as shown in figure 3.

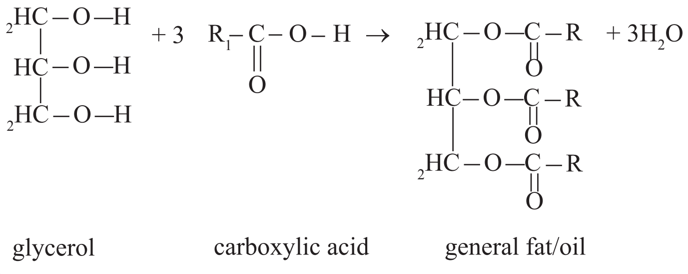
Fig. 3 A general esterification reaction



$$R_1-\underset{\underset{O}{\|}}{C}-O-H + H-O-R_2 \rightarrow R_1-\underset{\underset{O}{\|}}{C}-O-R_2 + H_2O$$

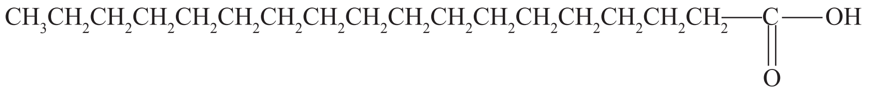
This is an example of a condensation reaction because two organic molecules are linked to form a larger organic molecule (the ester) as a result of the elimination of a small molecule (here it is water). Fats and oils are derived from the *same alcohol* in every case. This is the triol propan-1,2,3-triol (also known as glycerol). However, the carboxylic acids can vary to produce different fats and oils. Since the triol has 3 OH groups it can condense with 3 carboxylic acids to form a triester as shown in figure 4.

Fig.4 General fat / oil formation



The big difference between fats / oils and “ordinary esters” is the nature of the R groups. In fats and oils these tend to have ca. 12-24 carbon atoms. These long-chain carboxylic acids are often referred to as *fatty acids*. Furthermore, the R chain may or may not contain C=C double bonds. Those which do not contain C=C bonds are called *saturated fatty acids* while those that do are called *unsaturated fatty acids*. Examples are shown in figure 5.

Fig. 5 Some common fatty acids



$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2-C(=O)-OH$

[R = $C_{17}H_{35}$]

stearic acid octotadecanoic acid saturated

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH=CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2-C(=O)-OH$

[R = $C_{17}H_{33}$ with C=C at C9]

oleic acid octodec-9-enoic acid unsaturated

$CH_3CH_2CH_2CH_2CH_2CH=CHCH_2CH=CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2-C(=O)-OH$

[R = $C_{17}H_{33}$ with C=C at C9 and C12]

linoleic acid octadec-9,12-dienoic acid polyunsaturated

These differences are also carried over to the classify fats and oils. Those containing *only* saturated fatty acids are called *saturated fats*. The presence of *any* unsaturated fatty acids produces an *unsaturated fat*.

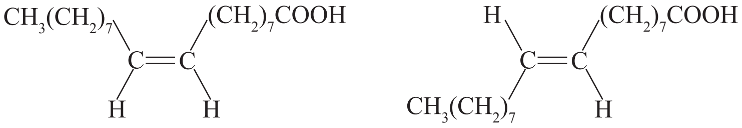
Finally, any combination of fatty acids can be present in a fat/oil. They can all be the same, all 3 different, all 3 saturated, all 3 unsaturated etc.

Fats versus oils

This depends on the effectiveness of the inter-molecular forces. Stronger inter-molecular forces result in a solid state (a fat) at room temperature whereas weaker inter-molecular forces result in a liquid state (an oil).

The inter-molecular forces are determined mostly by the degree of unsaturation and whether the C=C bonds (if present) in the fatty acids have a cis (Z) or trans (E) configuration. These configurations are shown in figure 6 for oleic acid.

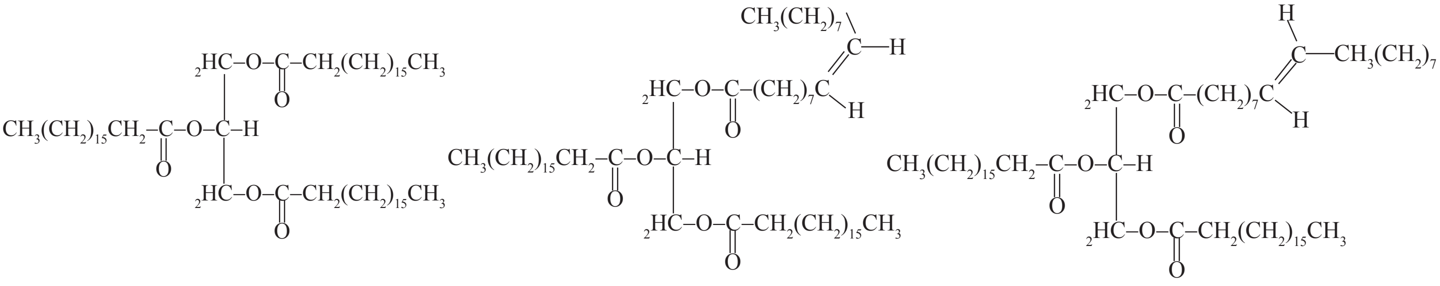
Fig. 6 Cis and trans fatty acids



cis-oleic acid *trans*-oleic acid

Because of the non-rotating nature of the C=C bond, cis configurations cause significant bends in the main carbon chain whereas trans configurations cause very little disturbance of the linearity of the main carbon chain. In fact, trans unsaturated fats are very similar in shape to saturated fatty acids. These shape differences are illustrated in figure 7.

Fig 7 General shapes of saturated and unsaturated fats



A saturated fat A cis unsaturated fat A trans unsaturated fat

The outcome is that "more linear" saturated and trans unsaturated molecules are better able to pack together making their inter-molecular forces more effective, resulting in them being solid (a "fat") at room temperature. Conversely, cis unsaturated molecules are less able to pack together making their inter-molecular forces less effective, resulting in them being liquid (an "oil") at room temperature.

In general, as the number of cis C=C bonds increases in the triester the inter-molecular forces will get weaker and weaker making the melting point get lower and lower.

Note : Trans unsaturated fats very rarely occur in nature!

Health issues

Because of their ability to pack together and form solid deposits, saturated and trans unsaturated fats are considered to present a risk of coronary heart disease. However, since the body is able to metabolize saturated fats, opinions about the level of risk have been less consistent in recent times. In contrast, trans fats are not as susceptible to metabolization as other fats and are considered to significantly increase the risk of coronary heart disease.

Measuring the degree of unsaturation of a fatty acid by titration

An accurately weighed sample of the fatty acid is reacted with excess iodine solution. Iodine molecules add across any C=C bonds and the *excess* of iodine is measured by titration against standard sodium thiosulphate ($Na_2S_2O_3$) solution using starch indicator.

Note 1: this is the *principle* of the method. In practice the procedure is much more involved.

Note 2: in practice, fats with various fatty acids are used giving what is called the *iodine number* of the fat.
This give a measure of the *overall* unsaturation with higher iodine numbers indicating more C=C bonds. e.g. Olive oils have an iodine number in the range 80-88 whereas sunflower oil is 125-144.

Note 3: this method is closely related to the bromine water test used to detect C=C bonds in organic molecules.
Orange bromine water is decolorized as bromine molecules add to C=C bonds.

e.g. 0.502g of a fatty acid with M_r 234 was reacted with $100.0cm^3$ of $0.100 \text{ mol dm}^{-3}$ iodine solution.
The unreacted iodine required $28.30cm^3$ $0.100 \text{ mol dm}^{-3}$ sodium thiosulphate for reaction.
Calculate the number of C=C bonds in one molecule of the fatty acid.

Moles $Na_2S_2O_3$ titrated $= 0.100 \times 28.30 / 1000 = 2.830 \times 10^{-3}$
This reacts with I_2 by $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$
$\rightarrow$ Moles I_2 **not** reacted with fatty acid $= \frac{1}{2} \times 2.830 \times 10^{-3} = 1.415 \times 10^{-3}$

Mole I_2 added to fatty acid initially $= 0.100 \times 100.0 / 1000 = 0.01$
$\rightarrow$ Moles I_2 **reacted** with fatty acid $= 0.01 - 1.415 \times 10^{-3} = 8.585 \times 10^{-3}$

Moles of fatty acid used $= 0.502 / 234 = 2.145 \times 10^{-3}$
$\rightarrow$ Molar ratio of reacting I_2 : fatty acid
$= 8.585 \times 10^{-3} / 2.145 \times 10^{-3}$
$= 4.002 : 1 = 4:1$ for simple whole number ratio

But each C=C bond in the fatty acid reacts with one mole of I_2
$R\text{-}CH{=}CH\text{-}R + I_2 \rightarrow R\text{-}CHI\text{-}CHI\text{-}R$
$\rightarrow$ Four C=C per molecule of fatty acid.

Hydrogenation of unsaturated fats

This is the process by which poly-unsaturated vegetable oils are converted to solid fats by addition of hydrogen to *some or all* of the C=C bonds in the presence of a finely divided nickel catalyst at about 150°C.

$$>C{=}C< + H_2 \rightarrow >CH\text{-}CH<$$

In general, the reaction time and temperature are controlled to give only *partial hydrogenation* of the oil. Some C=C bonds remain in the product, but enough are removed to ensure the product is in the solid state.

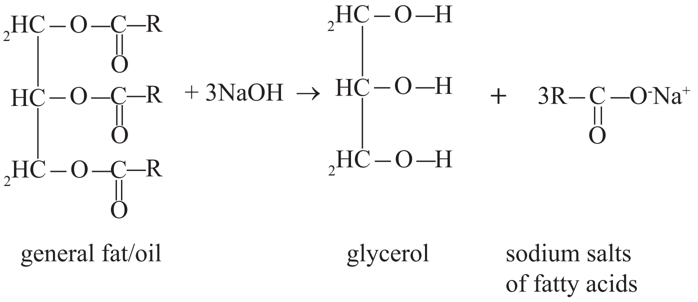
This process was first developed in the 1950's to produce *hard* margarine by complete hydrogenation. This provided a cheap substitute for butter. As *partial* hydrogenation was developed and applied, a wide range of "soft" spreadable margarines became available.

Unfortunately, in recent times, studies have shown that the advantages of these spreadable margarines are countered by the fact that, during hydrogenation, some of the naturally occurring cis configurations *isomerize* to trans configurations. As mentioned earlier, these trans fatty acids have been linked to an increased risk of coronary heart disease!

Making soap

This process is called *saponification*. Fats or oils are boiled with concentrated sodium hydroxide solution causing *hydrolysis* of the three ester linkages to produce a mixture of glycerol and the sodium salts of the component fatty acids as shown in figure 8.

Fig. 8 Soap Formation



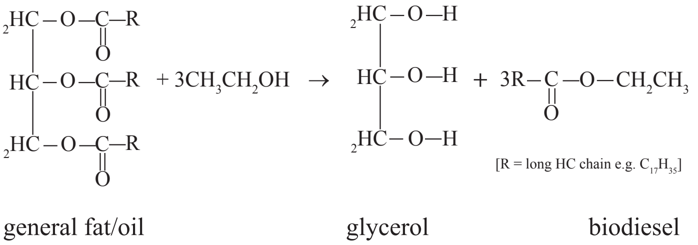
The ionic sodium salts are the *soaps* – substances which cause grease to be emulsified in water, allowing it to be washed away from the skin, dirty clothes etc.

The reaction mixture is treated with brine which causes the soaps to precipitate out. The remaining glycerol is a valuable raw material, particularly for cosmetic and pharmaceutical applications.

Making biodiesel

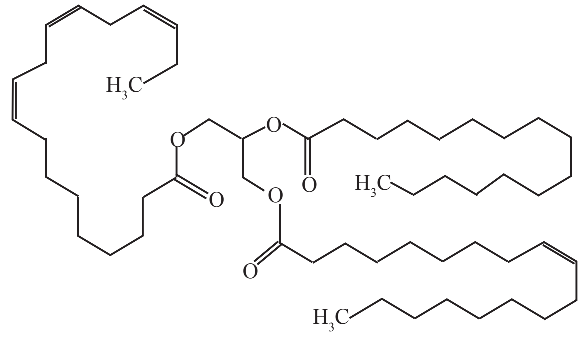
Biodiesel is a mixture of methyl or ethyl esters of fatty acids. It is made by a process called *trans-esterification* whereby natural fats / oils (e.g. rape seed) are reacted with methanol or ethanol in the presence of a little sodium hydroxide catalyst as shown in figure 9 for ethyl esters.

Fig. 9 Biodiesel Formation



It is a substitute for hydrocarbon diesel which, unlike petroleum oil, uses a *renewable resource*, produces *zero net carbon dioxide emissions* and zero emissions of pollutants such as SO_2.

Questions

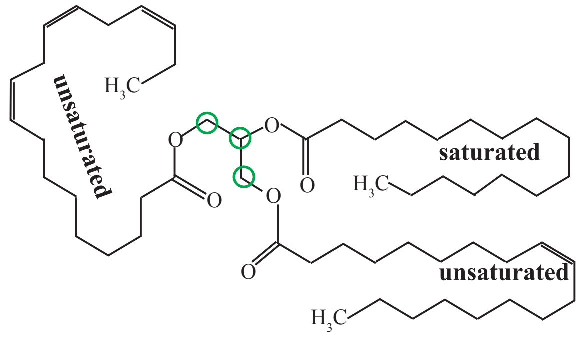


The questions which follow refer to the triglyceride shown above.

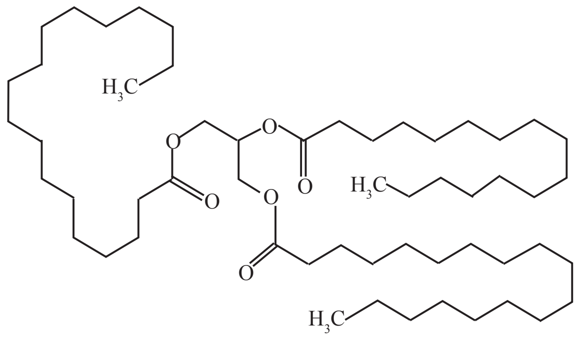
1. Draw circles around the 3 C atoms which are derived from glycerol.
2. Is this triglyceride best described as saturated, unsaturated or poly-unsaturated?
3. How many of the 3 fatty acids are saturated?
4. How many moles of iodine would react per mole of the triglyceride?
5. What reaction conditions would be adopted to hydrogenate this molecule?
6. Draw the structure of the fully hydrogenated triglyceride produced.
7. How could this triglyceride be saponified?
8. Draw the structure of the *saturated* soap produced by saponification.
9. Draw the structures of the different biodiesel molecules produced by the trans-esterification of this triglyceride with methanol.

Answers

1.



2. Poly-unsaturated because many C=C bonds are present.
3. One – see answer to question 1.
4. Four since each of the 4 C=C bonds reacts with one molecule of iodine.
5. React with hydrogen gas at about 150°C using finely divided nickel as a catalyst.
6.



7. Heated / boiled with concentrated sodium hydroxide. Brine then added to precipitate the soaps.
8. 15C in saturated R chain
   $\rightarrow CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COO^-Na^+$
9. (a) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOCH_3$
   (b) $CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2COOCH_3$
   (c) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2COOCH_3$

Acknowledgements: *This Factsheet was researched and written by Mike Hughes.*
Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ISSN 1351-5136