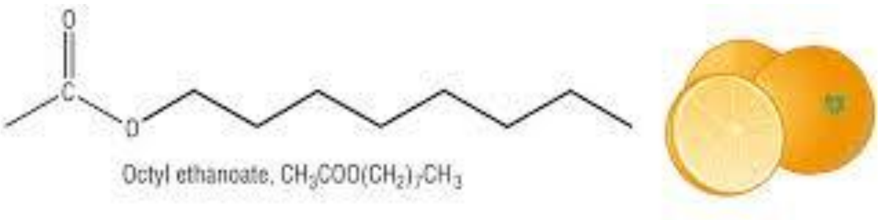
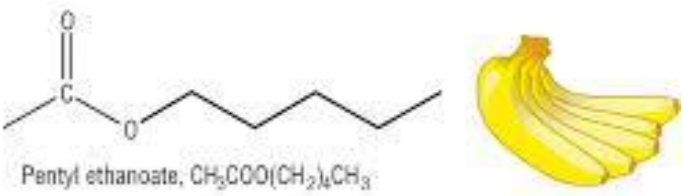
Cathkin High School
CfE Higher Chemistry

Nature's Chemistry
Esters, Fats and Oils





No.	Learning Outcome	Understanding?
1	An ester can be identified from the name containing the "-yl-oate" endings.	☺ 😐 ☹
2	An ester can be named given the names of the parent carboxylic acid and alcohol.	☺ 😐 ☹
3	Structural formulae for esters can be drawn given the names of the parent carboxylic acid and alcohol or the names of esters.	☺ 😐 ☹
4	Esters have characteristic smells and are used as flavourings, fragrances and industrial solvents.	☺ 😐 ☹
5	Esters are formed by the condensation reaction between a carboxylic acid and an alcohol.	☺ 😐 ☹
6	The ester link is formed by the reaction of a hydroxyl group with a carboxyl group.	☺ 😐 ☹
7	In condensation reaction the molecules join together with the elimination of water.	☺ 😐 ☹
8	Esters can be hydrolysed to produce a carboxylic acid and alcohol.	☺ 😐 ☹
9	In a hydrolysis reaction a molecule	☺ 😐 ☹

	reacts with water, breaking down into smaller molecules.	
10	Given the name of an ester or its structural formula, the hydrolysis products can be named and structural formulae drawn.	☺ 😐 ☹
11	Fats and oils in the diet supply the body with a more concentrated source of energy than carbohydrates.	☺ 😐 ☹
12	Fats and oils are essential for the transport and storage of fat soluble vitamins in the body.	☺ 😐 ☹
13	Fats and oils are esters formed from the condensation of glycerol and 3 carboxylic acids known as fatty acids.	☺ 😐 ☹
14	Fatty acids are saturated or unsaturated straight carboxylic acids containing even numbers of carbon atoms ranging from C_4 to C_{24}.	☺ 😐 ☹
15	The lower melting point of oils compared to those of fats is related to the higher degree of unsaturation of oil molecules.	☺ 😐 ☹
16	The lower melting points of oils are a result of the effect that the shapes of the molecules have on close packing, hence on the strength of van der Waals' forces of attraction.	☺ 😐 ☹

Esters

Esters are compounds made from alcohols and carboxylic acids. An example of an ester is ethyl ethanoate. An ester can be recognised from its name by the endings of the two parts of its name shown in bold e.g. ethyl ethanoate.

The first part of the name comes from the alcohol and the second part from the carboxylic acid. So ethyl ethanoate is made from the alcohol - ethanol and the carboxylic acid - ethanoic acid. Notice that in the name, the alcohol part is named first and the carboxylic acid second.

You will also be expected to identify and ester from its formula. This will be clearer when you look at 'Making Esters'. Within the structure is a functional group called the *ester link* (sometimes called the ester linkage) which has the formula -COO- (sometimes written as -CO.O-). The structure of the ester link has the carbon atom double bonded to one oxygen atom and also connected by a single bond to the other oxygen atom.

Ethyl ethanoate would have the shortened structural formula $CH_3COOC_2H_5$ (or $CH_3CO.OC_2H_5$). Notice that in the formula, the carboxylic acid part is usually (but not always) drawn first and the alcohol part second. The key to identifying the acid part of the ester is with the C=O bond (written as CO). In the above shortened formula, the CO is attached to CH_3 and comes from the 2-carbon acid called ethanoic acid.

Have a go at drawing the full structural formula of this ester.

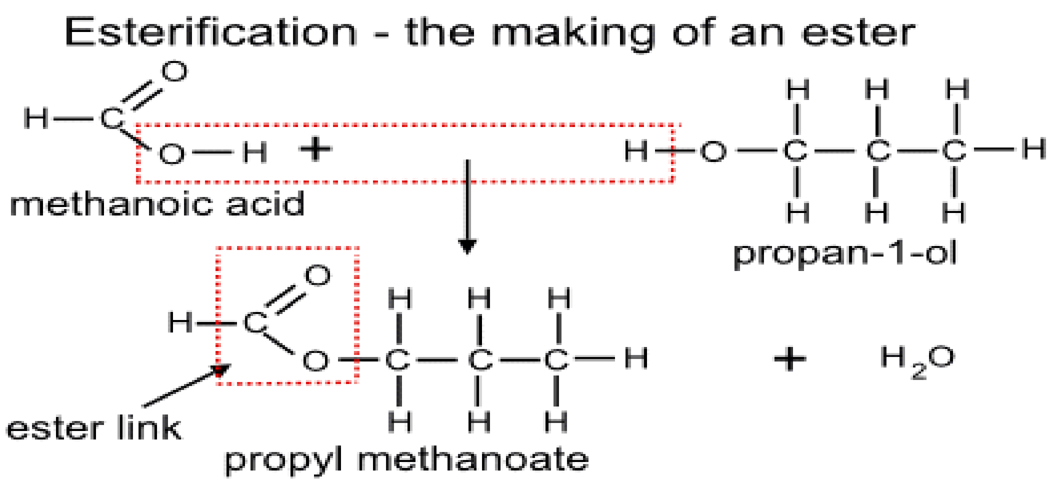
If another ester was drawn the 'other way round' it would look $CH_3OOCC_2H_5$. In this ester, the acid is on the RHS and is a 3-carbon acid made from propanoic acid, while the alcohol is a 1-carbon alcohol called methanol. This ester would be called **methyl propanoate**.

Have a go at drawing the full structural formula of this ester.

Making Esters

Esters are made by a *condensation reaction* between carboxylic acid and alcohol in which a molecule of water is eliminated. The hydroxyl group of the alcohol reacts with the carboxyl group of the carboxylic acid to eliminate the elements of water. This results in the formation of the ester link (-COO-) between the two molecules. This is shown in the reaction below.

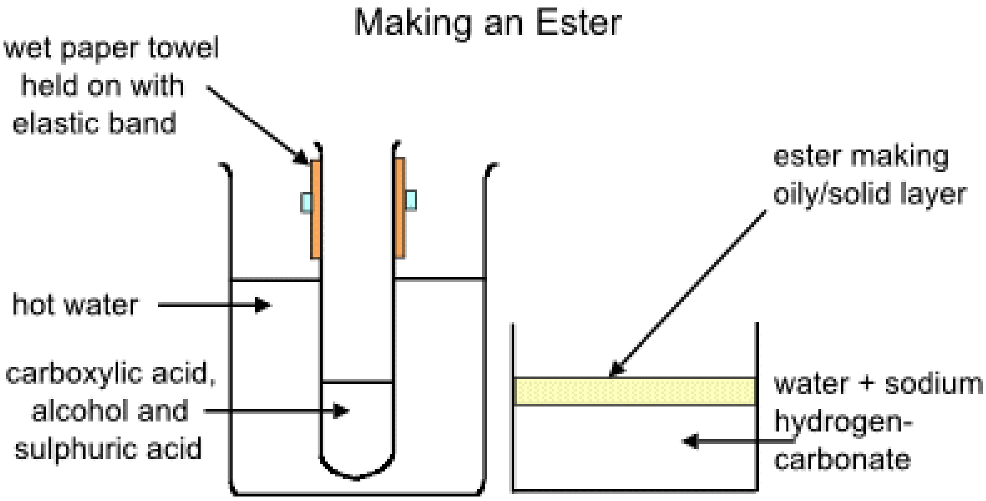
The making of an ester is called an *esterification* reaction.



The reaction to make a different ester can also be shown in simple equations.

$$C_3H_7COOH + HOC_2H_5 \rightleftharpoons C_3H_7COOC_2H_5 + H_2O$$

Notice that the arrow in the equation is reversible which means that the reaction can occur in both directions. More **information on this will be found in Unit 3.**



Esters are made by warming the carboxylic acid and alcohol in a test tube containing a few drops of concentrated sulphuric acid and heated by a water bath for about 10 minutes.

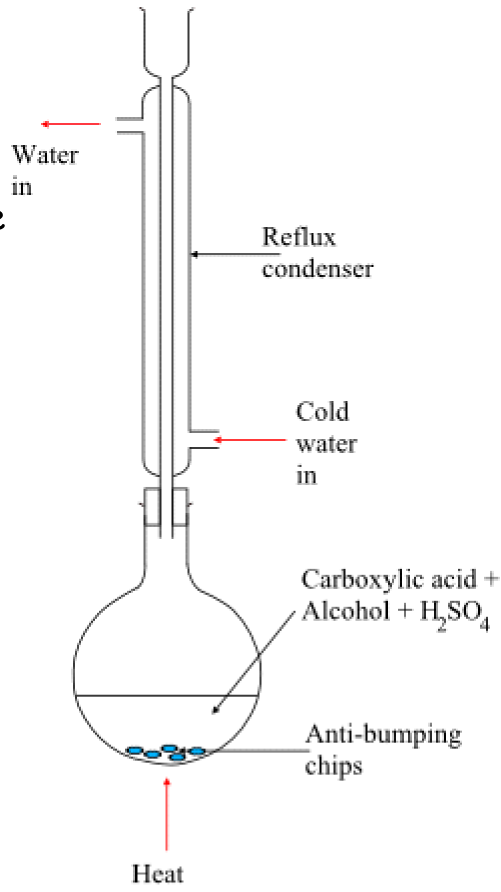
This prevents the reaction mixture catching fire. However, to prevent the reactants and products being lost during heating, a wet paper towel is wrapped around the outer, upper part of the test tube.

This causes volatile reagents to condense and run back into the test tube in a technique called *refluxing*

The process is reversible i.e. it operates in both directions.

Refluxing can also be done using the apparatus shown opposite. Anti-bumping chips help the liquid boil smoothly.

Sulphuric acid is a catalyst for the reaction and as a dehydrating agent; it removes the water that is formed.



By removing the water from the reaction, the reverse reaction is prevented, so that more ester is made.

The ester is obtained by pouring the mixture into a beaker containing an aqueous solution of sodium hydrogencarbonate to neutralise the sulphuric acid.

Evidence that an ester is formed is its typical smell, and that is appears as a solid/oily liquid on the water.

Uses of esters as food flavourings

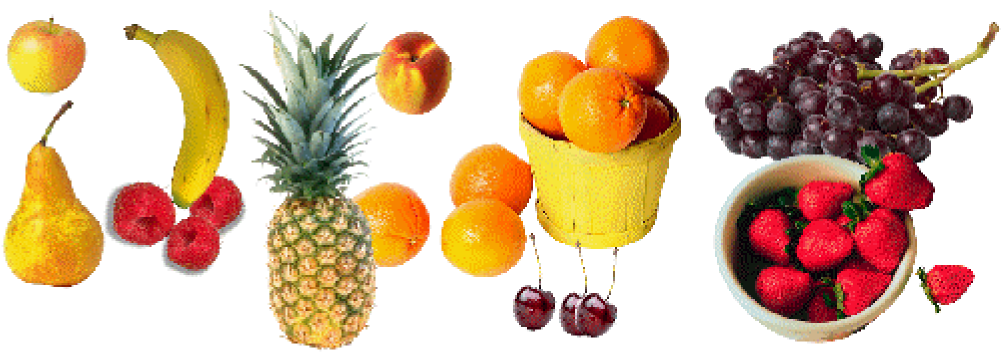
Many esters are found in fruits and are also used in flavouring foods.

They are also used in fragrances e.g. benzyl ethanoate. Natural pheromones from insects such as the bee are esters.

The following table gives the names and smells of some esters

Ester name	Shortened Molecular Formula	Alcohol used	Carboxylic acid used	Smell
Methyl butanoate	$C_3H_7COOCH_3$	Methanol	Butanoic acid	Apple
Benzyl butanoate	$C_3H_7COOCH_2C_6H_5$	Benzyl alcohol	Butanoic acid	Cherry

Benzyl ethanoate	$CH_3COOCH_2C_6H_5$	Benzyl alcohol	Ethanoic acid	Peach, flowers
Methyl salicylate (or methyl 2-hydroxybenzoate)	$C_6H_4(OH)COOCH_3$	Methanol	Salicylic acid (or 2-Hydroxybenzoic acid)	Oil of wintergreen
Octyl ethanoate	$CH_3COOC_8H_{17}$	Octanol	Ethanoic acid	Orange
Propyl ethanoate	$CH_3COOC_3H_7$	Propanol	Ethanoic acid	Pear
Ethyl methanoate	$HCOOC_2H_5$	Ethanol	Methanoic acid	Rum flavouring
Propyl pentanoate	$C_4H_9COOC_3H_7$	Propanol	Pentanoic acid	Pineapple
2-Methylpropyl methanoate	$HCOOCH_2CH(CH_3)CH_3$	2-Methylpropan-1-ol	Methanoic acid	Raspberry
Pentyl butanoate	$C_3H_7COOC_5H_{11}$	Pentanol	Butanoic acid	Apricot, Strawberry
Methyl anthranilate (or methyl 2-aminobenzoate)	$C_6H_4(NH_2)COOCH_3$	Methanol	2-Aminobenzoic acid	Grapes



Some fruits contain esters

Uses of esters as solvents

Ethyl ethanoate is one of a number of solvents used to extract caffeine from coffee and tea. De-caffeinated products produced with ethyl ethanoate are often described on the packaging as "naturally decaffeinated" because ethyl ethanoate is a chemical found naturally in many fruits. You may have the opportunity to extract caffeine from tea or coffee. If you do this experiment you will be able to get an idea of the percentage by mass of caffeine in the tea or coffee which can be calculated from

$$\frac{\text{mass of caffeine}}{\text{mass of tea or coffee}} \times 100$$

Esters are *non-polar* solvents and are able to dissolve many materials that water, a polar solvent, cannot dissolve. Esters are used as solvents for dyes, glues, inks as in permanent markers and whiteboard markers, nail varnish removers, car spray paints and varnishes.

One problem in using *volatile* esters as solvents is that evaporation leads to high concentrations of esters in the air.

The move to reduce the use of esters as solvents can be found by searching for "VOC reduction" or "low VOC" on an internet search engine. *VOC* stands for 'volatile organic compound'. The term VOC is often found on the labelling of paints described as low VOC paints.

Hydrolysis of Esters

When an ester is added to water or heated with water it begins to break down into a carboxylic acid and alcohol. This reaction is easy to show by testing the pH of the solution with pH paper. The acid made in the reaction will cause the pH to decrease.

This breaking down reaction with water is called *hydrolysis* and it is the exact opposite of condensation. You will be expected to name and/or draw the structural formulae of the carboxylic acids and alcohols made from specific esters. If you are uncertain, look back to the equation that shows an ester being made. You would want the reverse of this reaction. Also the table of esters used as flavourings also shows you the name of the parent carboxylic acid and alcohol.

It is not possible by this method to totally break down all of the ester and the reaction mixture will contain some ester, water, carboxylic acid and alcohol.

The reaction by be speeded up using H^+ ions or OH^- ions. If an alkali is used, this further helps by reacting with the carboxylic formed in the hydrolysis and removing the carboxylic acid from the reaction.
This prevents the joining of the alcohol with the carboxylic acid to remake the ester.

This idea of manipulating reversible reactions will be dealt with in Unit 3 of the course.

Fats and Oils

Natural fats and oils can be classified according to their origin as animal, vegetable or marine.

Animal	Vegetable	Marine
Beef fat	Sunflower oil	Cod liver oil
Pork fat	Olive oil	Tuna fish oil
Sheep fat	Linseed oil	Whale oil
Butterfat	Palm oil	Halibut liver oil

Fats are also classed as solids while oils are classed as liquids.

Fats and Oils in the Diet

Fats and oils in the diet supply the body with energy and are a more concentrated source of energy than carbohydrates e.g. bread flour (mostly carbohydrate) contains 1420 kJ per 100g while vegetable oil contains 3700 kJ per 100g.

Your teacher may demonstrate an oil fire and may also show you why you should never put water on an oil fire.

We eat too much fat/oil, though there is evidence that unsaturated oils are less harmful than saturated fats.

Fats and oils are essential for the transport and storage of fat soluble vitamins in the body. Vitamins are divided into two groups: water-soluble (B-complex and C) and fat-soluble (A, D, E and K).

The following table is provided for reference only. The information included is not needed in the course.

Vitamin	**Role in the body**	**Additional role**	**Consequence of shortage**
A	Eye function	Keeping nose, throat moist	Night blindness, throat infections
D	Formation of strong bones	Helps the uptake of calcium	Rickets (weak bones)
E	Protects vitamin A and C	Anti-oxidant	Deficiency is rare
K	Helps with blood clotting	-	Excessive bleeding

Unlike water-soluble vitamins that need regular replacement in the body, fat-soluble vitamins are stored in the liver and fatty tissues, and are eliminated much more slowly than water-soluble vitamins.

Other uses of oils

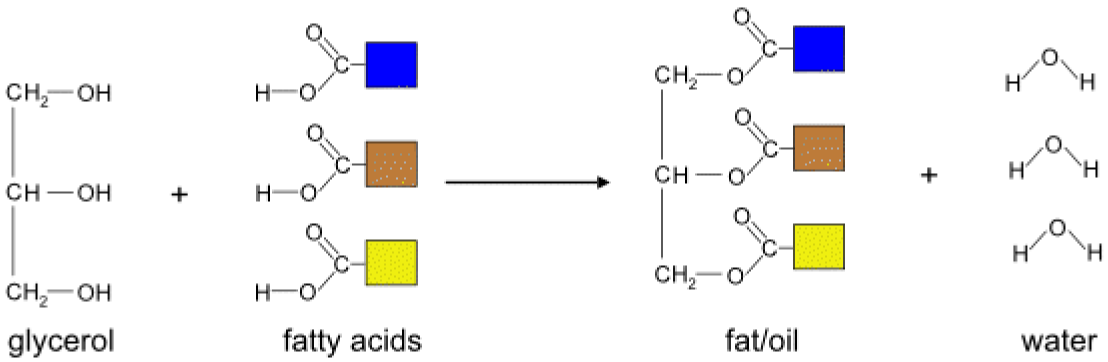
Some edible oils are used as fuels such as bio-diesel and this is more important as fuels from crude oil become scarcer and more expensive.

Also lubricants for some agricultural machinery are made from vegetable oil in order to prevent any risk of harmful mineral oils (i.e. those from crude oil) contaminating future food stuffs.

Structure of Fats and Oils

Fats and oils are esters made when an alcohol, *glycerol* (with 3 hydroxyl groups) condenses with carboxylic acids known as fatty acids.
Glycerol (propane-1,2,3-triol) is a *trihydric alcohol*.

The reaction between three fatty acids and glycerol is shown below.



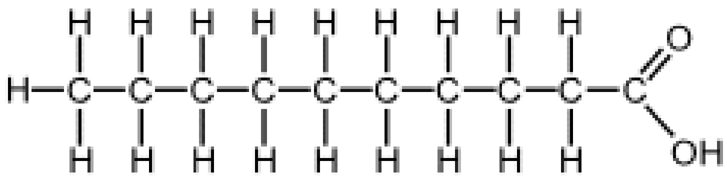
Each molecule of the alcohol condenses with 3 molecules of fatty acid.

The hydrolysis of fats and oils produces fatty acids and glycerol in the ratio of three moles of fatty acid to one mole of glycerol.

Structure of Fatty Acids

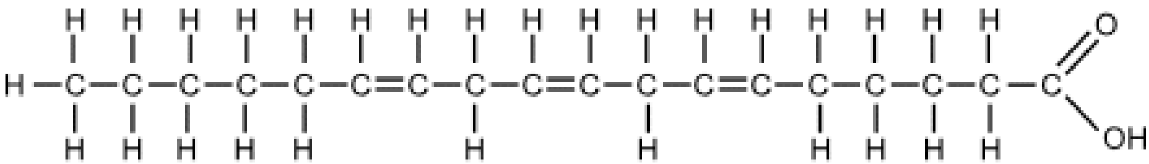
Fatty acids **are saturated or unsaturated straight-chain carboxylic acids containing even numbers of carbon atoms ranging from C_4 to C_{24}, primarily C_{16} and C_{18}.**

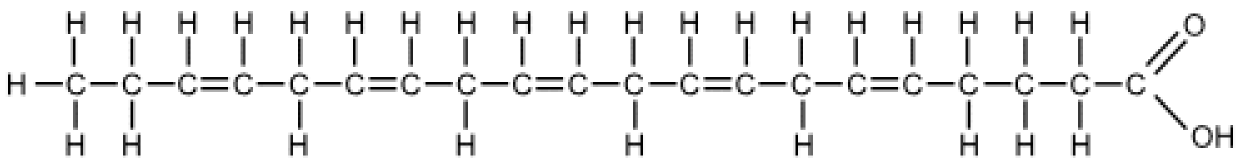
Fatty acid	Molecular formula	Saturated/Unsaturated
Butanoic acid	C_3H_7COOH	Saturated
Stearic acid	$C_{17}H_{35}COOH$	Saturated
Oleic acid	$C_{17}H_{33}COOH$	Unsaturated
Linoleic acid	$C_{17}H_{31}COOH$	Unsaturated



Capric acid is a fatty acid found in goat's milk. It is a completely saturated fatty acid

Examples of two unsaturated fatty acids are shown below.





Fats and oils consist largely of mixtures of *triglycerides* in which the three fatty acid molecules which are combined with each molecule of glycerol may or may not be identical.

A greater proportion of the fatty acid molecules in fats are saturated, particularly in hard fats such as beef fat.

Degree of Unsaturation in Fats and Oils

When an oil is shaken with bromine water, the brown colour of bromine water is lost rapidly. This indicates the presence of double bonds in the oil molecules.

If a fat is dissolved in an organic solvent such as hexane and then shaken with bromine water, no decolourisation occurs with some fats and only slight or slow decolourisation with others.
This indicates that fats may contain no double bonds or fewer double bonds than oils.

It is possible to *titrate* fats/oils against bromine water and to determine the volume (and hence the number of moles) of bromine needed to react with all of the double bonds in 1 mole of the fat/oil molecules. A simpler way to establish the degree of unsaturation of an oil is to count the number of drops of bromine water that have to be added until no further decolourisation occurs. The greater the number of drops, the more unsaturated the oil. The end-point is when all of the double bonds have been used up and a trace of bromine (brown colour) remains.

Each double bond will react with 1 molecule of bromine or each mole of double bonds will react with 1 mole of bromine.

Fat/Oil	No. of moles of fat/oil	No. of moles of bromine	Equivalent no. of moles of double bonds
Beef fat	1	0	0
Sunflower oil	1	6	6
Pork fat	1	1	1
Whale oil	1	3	3

Oils decolourise more bromine than fats because they are more unsaturated. Marine oils are more unsaturated that other animal fats.

Degree of unsaturation of fats and oils using iodine (Wij's method)

Another titrimetric measurement is called the iodine number or value. Iodine values can be determined by standard methods including the use of Wij's reagent.

An excess of a solution of iodine monochloride (Wij's reagent) adds rapidly to the carbon-carbon double bonds present.

A simplified equation is shown below. R and R' represent parts of the molecule not involved in the reaction

$$R - CH = CH - R' + I - Cl \longrightarrow R - CH(I) - CH(Cl) - R'$$

A known mass of fat or oil is used together with 1,1,1-trichloroethane (or CCl_4 or $CHCl_3$) to dissolve it. It is treated with a known volume of Wij's reagent and the mixture kept in the dark for about 1 hour for the addition reaction to take place. ICl is sensitive to light.

An excess of potassium iodide solution is added which reacts with the excess Wij's reagent and iodine, I_2 is made.

$I - Cl + I^-(aq) \longrightarrow I_2 + Cl^-(aq)$

The liberated iodine is determined by titration with standard sodium thiosulphate solution.

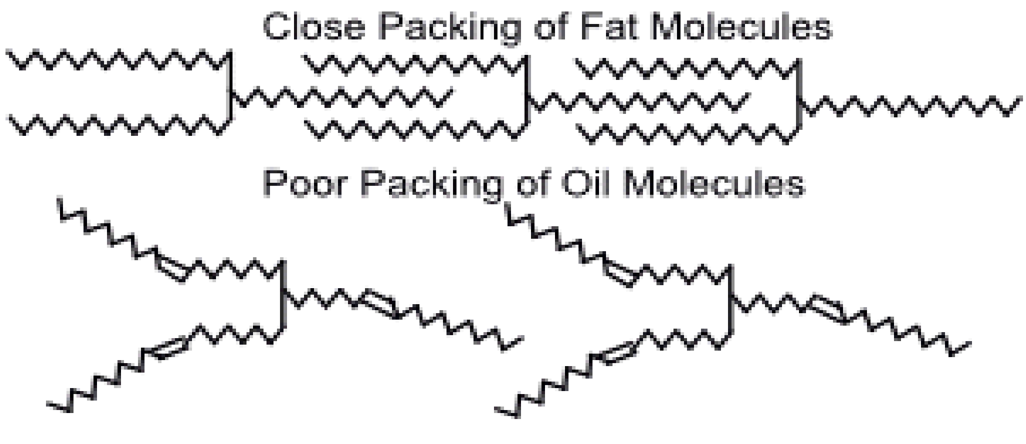
$I_2(aq) + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}(aq)$

It is then possible to calculate the amount of iodine that reacted with the original fat or oil and the answer called the iodine value is usually expressed as grams iodine/100 grams of fat or oil. The higher the value, the more unsaturated the fat or oil.

Melting Points of Fats and Oils

The lower melting points of oils compared to those of fats is related to the higher unsaturation of oil molecules.

The presence of double bonds in oil molecules causes the long chains of atoms to become distorted.
This stops the oil molecules packing as closely together as the more saturated fat molecules can.



The poorer packing means less London dispersion forces can form between oil molecules than between fat molecules.
Less heat energy is needed to separate oil molecules and oils have lower melting points than fats.

Proteins - Glossary

Word	Meaning
Ester Link	A group of atoms of formula -COO- found in ester molecules and made from the combination of the carboxyl group and the alcohol group.
Condensation Reaction	A reaction where two or more molecules join together and a small molecule, usually water is eliminated.
Esterification	A condensation reaction where an ester is made.
Reflux	Where liquid evaporate to form gases which are then re-condensed to continue reaction.
Non-Polar	Describes a molecule where any charges are insignificant or absent.
Volatile	Describes a liquid which evaporates readily i.e. changes to a gas easily
VOC	Volatile organic compound.
Hydrolysis Reaction	A reaction in which a molecule is broken into smaller pieces using water.
Titrate	A process using pipette and burette where volumes of reactants can be accurately measured.
Vitamin	a chemical needed in small amounts with an essential role in the body and.
Glycerol	The trivial name for the alcohol propane-1,2,3-triol found in fats and oils.
Fatty Acid	A carboxylic acid with between 4 and 24 (but usually 16 or 18) carbon atoms in the molecule and found in fats and oils. Only even numbers of carbon atoms are found.
Trihydric Alcohol	An alcohol with three hydroxyl (-OH) groups in one molecule.

Word	Meaning
Triglyceride	The chemical name for a fat or oil i.e. an ester of glycerol and three fatty acid molecules.