CHAPTER

16 From fats and oils to soaps and biodiesel

The industrial production of many chemical substances requires the use of large amounts of raw materials. These raw materials, called feedstocks, are often obtained from naturally occurring sources.

Fats and oils are one such feedstock. The production of soap and biodiesel from fats and oils makes use of organic reactions, some of which you will have encountered already. When the processes are used on an industrial scale, scientists have to consider issues such as sustainability and the environment alongside economics and profitability. The principles of green chemistry can be used to inform choices around the conditions and reagents used in the processes.

At the end of this chapter, you will be able to describe how soaps are made, how soaps and detergents clean and how to determine the structure of the soap molecule(s) produced from a given fat or oil.

You will also learn about the manufacture of biodiesel and the transesterification reaction in base-catalysed and enzyme-catalysed processes. The advantages and disadvantages of each process will be highlighted.

Science as a human endeavour

- Scientific knowledge can be used to design alternative chemical synthesis pathways, taking into account sustainability, local resources, economics and environmental impacts (green chemistry), including the production of ethanol and biodiesel

Science understanding

- Chemical synthesis to form products with specific properties may require the construction of reaction sequences with more than one chemical reaction and involves the selection of particular reagents and reaction conditions in order to optimise the rate and yield of the product
- The base hydrolysis (saponification) of fats (triglycerides) produces glycerol and the salt of a long chain fatty acid (soap)
- The structure of soaps contains a non-polar hydrocarbon chain and a carboxylate group; the structure of the anionic detergents derived from dodecylbenzene contains a non-polar hydrocarbon chain and a sulfonate group

16.1 Fats and oils

SOURCES OF FATS AND OILS

'Fat' is a name used to describe a number of organic compounds belonging to a larger class of biological molecules called **lipids**. Fats and oils are the best-known types of lipids. Compounds such as waxes and steroids (which include cholesterol) are also members of the lipid family.

Fats and oils are typically obtained from either plant or animal sources. Animal fats tend to exist as solids at room temperature. They are mainly **saturated** fats—all the carbon–carbon bonds are single bonds.

Olive oil, canola oil and palm oil are common plant oils. They usually exist as liquids at room temperature. Plant oils are mainly **unsaturated** fats—they contain one or more double or triple carbon–carbon bonds.

STRUCTURE OF FATS AND OILS

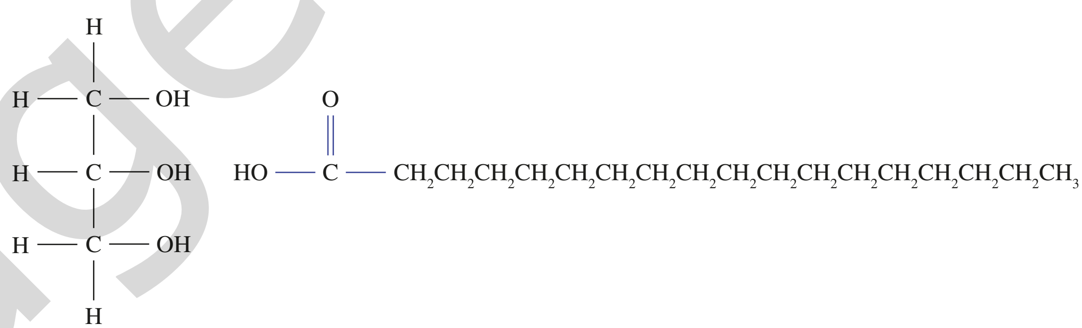
Fats and oils contain large **non-polar** molecules known as **triglycerides**. Non-polar molecules have no overall dipole present in the molecule. Fats and oils have similar chemical structures and are distinguished simply on the basis of their physical state at room temperature. At room temperature:

- fats are solids
- oils are liquids.

Being non-polar, triglycerides are unable to form hydrogen bonds with water, so fats and oils are insoluble in water.

General structure of a fatty acid and glycerol

Triglycerides are synthesised by condensation reactions between a glycerol molecule and three **fatty acids**. Fatty acids are carboxylic acids with chain lengths of eight or more carbons atoms. Glycerol (propane-1,2,3-triol) is a relatively small molecule with three hydroxyl functional groups (Figure 16.1.1). Fatty acids have a carboxyl functional group attached to a long unbranched hydrocarbon chain, or 'tail'. This tail makes up the bulk of the molecule. Most fatty acids have an even number of carbon atoms, usually between eight and 20 (Figure 16.1.1).



glycerol

fatty acid (stearic acid)

FIGURE 16.1.1 A glycerol molecule and a fatty acid molecule

Condensation reactions to form triglycerides

A condensation reaction can occur between an organic acid that contains a carboxyl group (–COOH) and an alcohol that contains a hydroxyl group (–OH). An **ester functional group** (–COO–) is formed, linking the two molecules. A molecule of water is also produced. You encountered condensation reactions in Chapter 14; reviewing the formation of esters in section 14.3 will help you to understand the chemical processes in this chapter.

When a small molecule, such as water, is produced in a reaction as a by-product, the reaction is said to be a condensation reaction.

A triglyceride is produced by a condensation reaction that involves the carboxyl group of a fatty acid and a hydroxyl group of glycerol, forming an **ester link** (this is highlighted in green in Figure 16.1.2). During a condensation reaction involving one glycerol molecule and three fatty acids, three ester links form and three molecules of water are released. This process is shown in Figure 16.1.2.

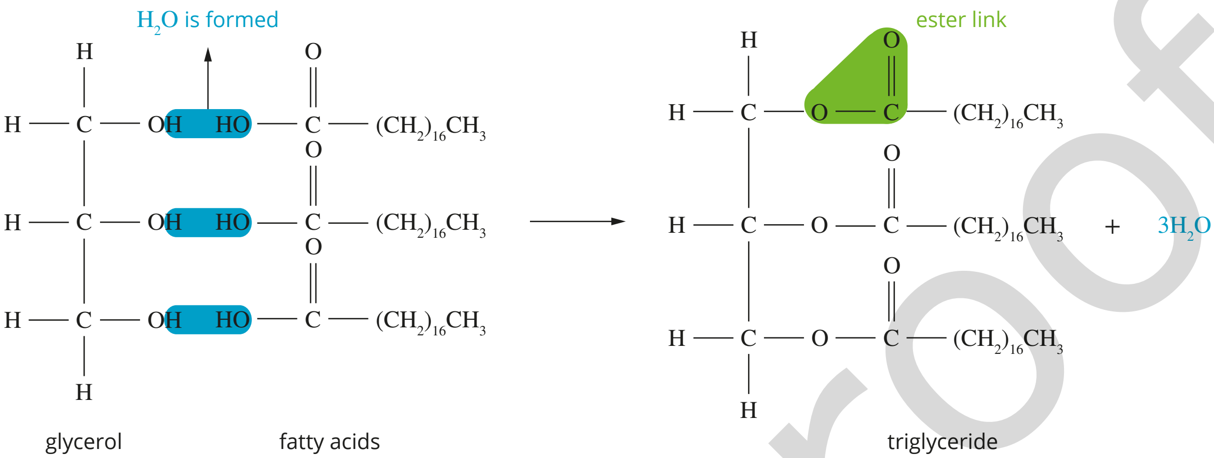


FIGURE 16.1.2 The reaction between glycerol and fatty acids produces a triglyceride and water.

In the example in Figure 16.1.2, the three chains on the triglyceride are identical, but triglycerides can often have two or three different fatty acid hydrocarbon chains that can differ in length. Some hydrocarbon chains may also contain one or more carbon–carbon double bonds.

SATURATED AND UNSATURATED FATTY ACIDS

Fats are classified according to the structural features of the hydrocarbon chains of their fatty acid components.

- Saturated fatty acids have hydrocarbon chains that contain only single carbon–carbon bonds. Stearic acid, which occurs widely in meats, has a structural formula of $CH_3(CH_2)_{16}COOH$.
- Monounsaturated fatty acids contain one carbon–carbon double bond in their hydrocarbon chain. The main dietary example is oleic acid, which is found in a number of vegetable oils. Its structural formula is $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$.
- Polyunsaturated fatty acids contain more than one carbon–carbon double bond in their hydrocarbon chain. Fish and vegetable oils are the main dietary source of polyunsaturated fatty acids. Linoleic acid, which occurs in sunflower oil, has the structural formula $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$.

The structure and general formula of stearic acid, oleic acid and linoleic acid are shown in Figure 16.1.3.

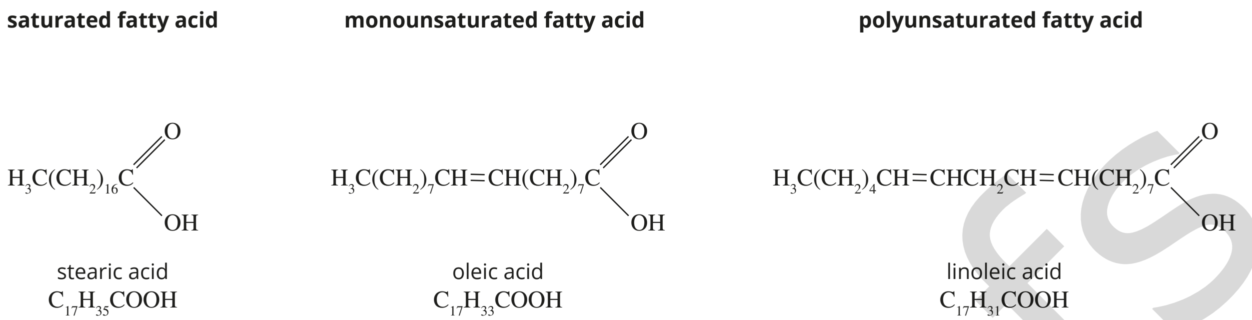


FIGURE 16.1.3 Examples of a saturated fatty acid, monounsaturated fatty acid and polyunsaturated fatty acid

USES OF FATS AND OILS

Fats and oils have a wide variety of uses, but the majority of applications are in food and related industries. Globally, this accounts for about 75% of production. The fats and oils may be used directly in food, as an ingredient, for frying food or as a fuel for cooking.

The other 25% of global production is used as a raw material to make new substances. Table 16.1.1 shows some other uses for oil and fats. Note that the predominant non-food uses by volume are in the production of **soap** and for manufacturing **biodiesel** (approximately 20%). Biodiesel is a fuel that can be used in vehicle engines and is made from fats and oils. These two important uses of fats and oils will be explored further in the remainder of this chapter.

TABLE 16.1.1 Non-food uses of fats and oils

End use	Oil or fat used
Paints	Soybean oil
Inks	Soybean oil
Candles	Hydrogenated vegetable oils
Pharmaceuticals, e.g. pill formulations	Various vegetable oils
Thermoplastics	Linseed
Cosmetics, e.g. lipstick	Olive oil, cocoa butter
Soap	Tallow, olive oil, palm oil and others
Biodiesel	Palm, canola, sunflower, tallow and others

16.1 Review

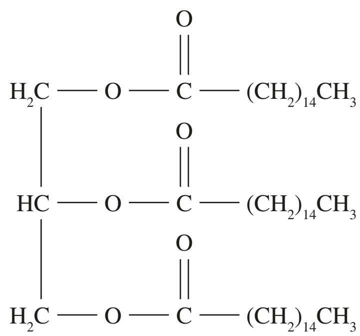
SUMMARY

- Oils and fats come from animal and plant sources.
- Animal fats are typically saturated fats.
- Plant oils are typically unsaturated fats.
- Fats and oils are triglycerides, which are molecules with three ester groups.
- Triglycerides can be synthesised from fatty acids and glycerol.
- Fats and oils are used in the food industry and in the manufacture of soap and biodiesel.

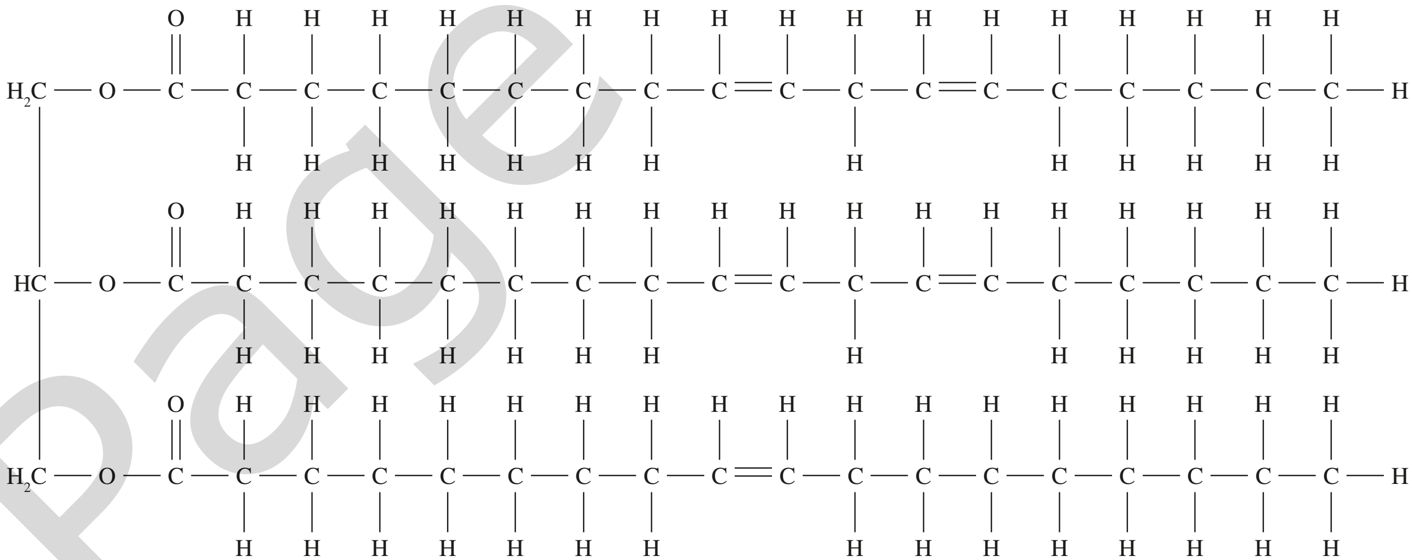
KEY QUESTIONS

1 Identify the most likely source, either animal or plant, for the following triglycerides and give an explanation for your choices.

a



b



2 For each of the structures in Question **1**, identify the ester groups in each molecule.

3 Draw the two molecules that form the fat given in Question **1a**.

16.2 Production of soaps

In the previous section, you were introduced to triglycerides (triesters) and their constituents, namely fatty acids (long chain carboxylic acids) and glycerol (an alcohol with three –OH groups). In Chapter 14 you learnt how esters can be hydrolysed, and that hydrolysis with strong bases will produce a salt of the carboxylic acid and the alcohol that form the ester. This knowledge is important in understanding the process of manufacturing soaps from oils.

SAPONIFICATION

Soap molecules contain a long hydrocarbon chain attached to a charged end. The structure of sodium stearate, a common soap, is shown in Figure 16.2.1.

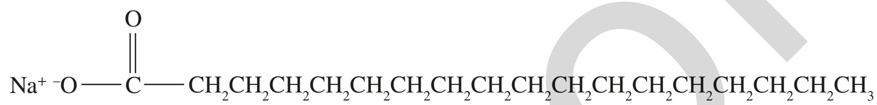


FIGURE 16.2.1 The formula of sodium stearate, a typical soap

To synthesise soap from a triglyceride, the ester bonds must be broken. In theory, water can be used for this reaction. Reactions in which water is used to break down a compound are known as **hydrolysis** reactions. In practice, the reaction with water is very slow, so a strong base such as sodium hydroxide or potassium hydroxide is used. The reaction with water under alkaline conditions is known as **base hydrolysis**. When base hydrolysis is applied specifically to esters, it is called **saponification** (Figure 16.2.2).

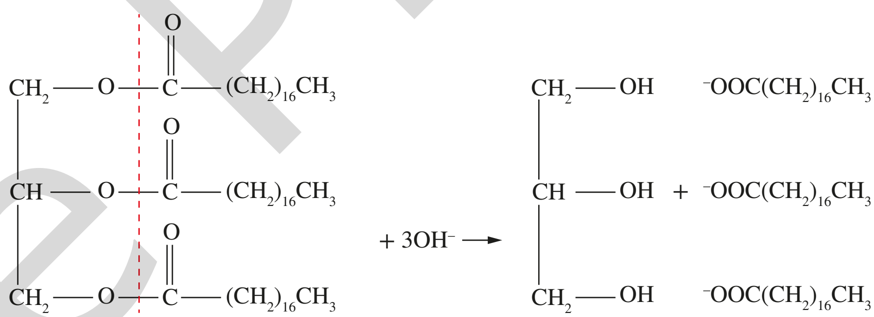


FIGURE 16.2.2 Base hydrolysis breaks the three ester bonds on the triglyceride along the dotted red line.

It is the fatty acid ion, combined with the metal ion from the base used for hydrolysis, that makes up the soap. For example, the soap potassium stearate (Figure 16.2.3) is formed when the triglyceride in Figure 16.2.2 reacts with potassium hydroxide.

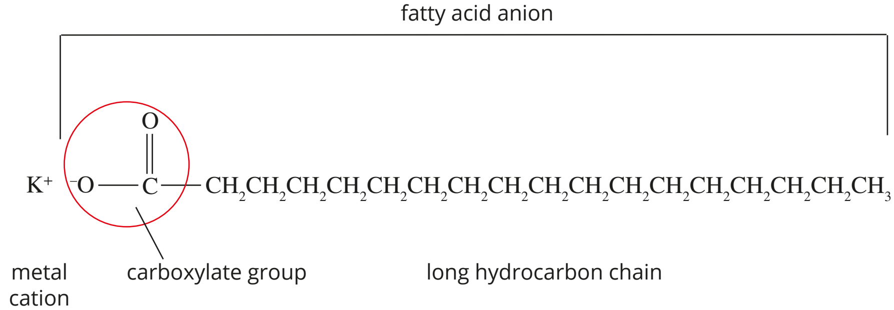


FIGURE 16.2.3 A soap, potassium stearate. Potassium stearate is described as the potassium salt of stearic acid.

All soaps are made up of a:

- long hydrocarbon chain. This part of the soap is non-polar. In potassium stearate (Figure 16.2.3), the hydrocarbon chain is an alkyl group because the hydrocarbon is saturated.
- **carboxylate** ion (COO^-) attached to the hydrocarbon tail. This is often referred to as the 'head' of the soap and is **polar**, meaning there is an uneven distribution of charge in this part of the soap. Carboxylate ions are the conjugate bases of carboxylic acids. In Figure 16.2.3, the stearate ion is the conjugate base of stearic acid ($CH_3(CH_2)_{16}COOH$).
- metal ion, normally Na^+ or K^+.

An alternative representation of the anion of a soap is shown in Figure 16.2.4.

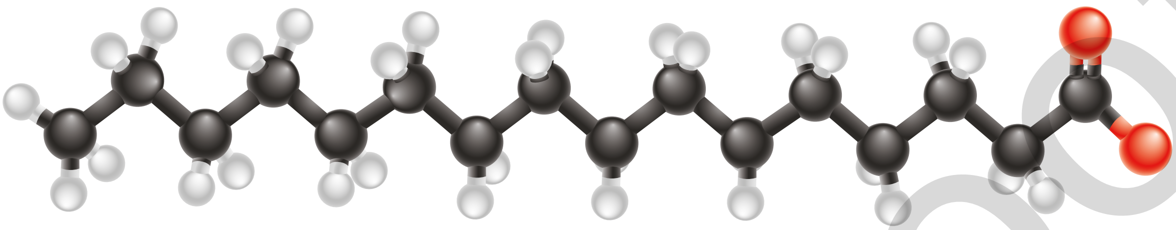


FIGURE 16.2.4 This alternative representation of the structure of a fatty acid anion in a soap uses coloured spheres for atoms (white for hydrogen, black for carbon and red for oxygen).

Even if a pure source of oil is used, the fatty acids in the triglyceride can vary. For this reason, in the general equation for saponification, chemists often represent the fatty acid hydrocarbon groups as R, R′ and R″, as shown in Figure 16.2.5.

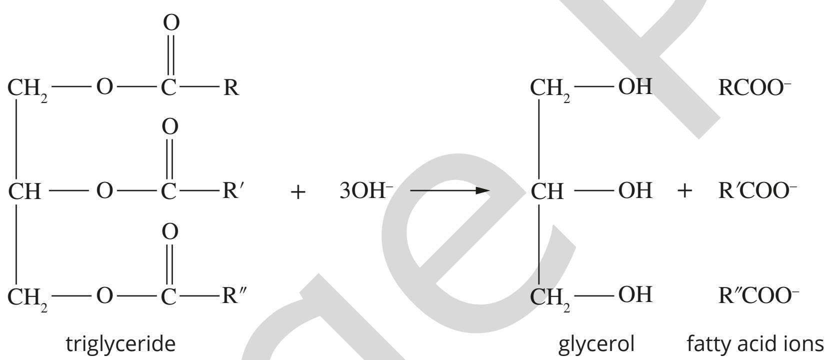


FIGURE 16.2.5 General equation for hydrolysis of a triglyceride. R, R′ and R″ represent different hydrocarbon groups.

SOAP PRODUCTION

Soap manufacturers usually select a triglyceride that is readily available in their region. Palm oil is popular in Asian countries and olive oil is widely used in southern Europe.

Soap can be made in a school laboratory by heating a mixture of a suitable fat or oil with concentrated sodium hydroxide solution. The product is rinsed with water, which removes most of the glycerol and any residual sodium hydroxide. The soap may then be dried and moulded to shape. The laboratory process is very similar to that used by small soap manufacturers who use a traditional batch process. A batch process is one where reactants are placed in a vessel, the reaction takes place over a period of time and then the products are removed.

Industrial production of soap, as shown in Figure 16.2.6, is performed in enormous vats at high temperature and uses continuous processes. Continuous processes are ones where products are removed as reactants are being added to continue the reaction process.

High temperatures ensure the hydrolysis of all the oil present. This means all of the oil added is converted to soap. Soap is precipitated through the addition of sodium chloride and then removed by filtration. The remaining solution from the reaction is also removed and the glycerol is separated from the basic solution. While soap and glycerol are being removed, more oil and hydroxide is being added to the vat so that the saponification reaction continues.

Manufacturers vary the amounts and types of perfumes, stabilisers and other additives to give their product desirable properties such as antibacterial and moisturising actions.

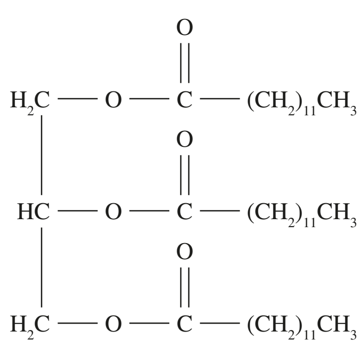
FIGURE 16.2.6 A soap production assembly line.

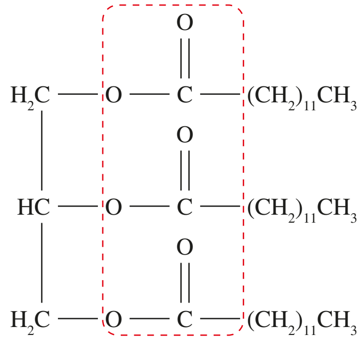
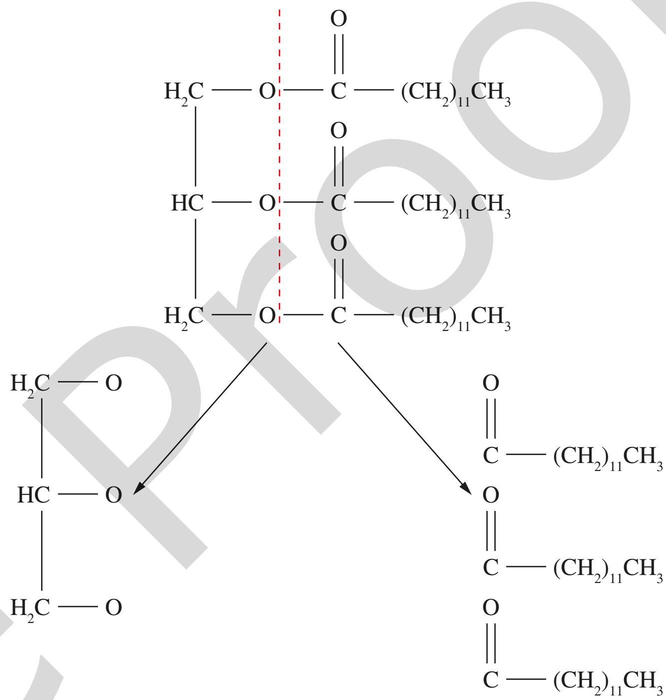
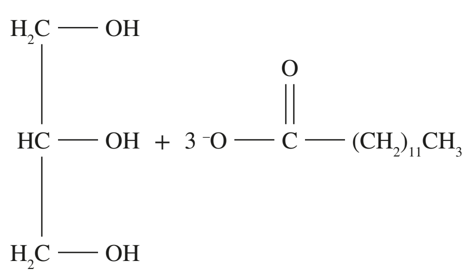
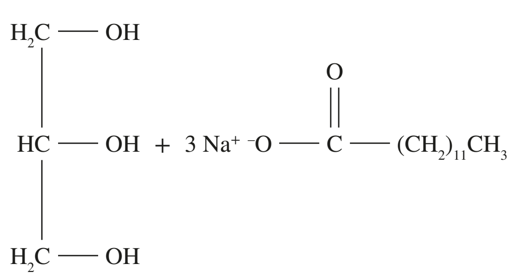
A by-product of soap manufacture is glycerol. Some soap manufacturers like to retain it in the soap to improve the moisturising properties, while others separate it out to use for other purposes. Glycerol is a common ingredient in the manufacture of gums and resins, paints, explosives and laxatives.

Worked example 16.2.1

DETERMINING THE PRODUCTS OF SAPONIFICATION FROM A TRIGLYCERIDE

The following triglyceride was reacted with sodium hydroxide to form a soap, sodium laurate. Give the products of this reaction.

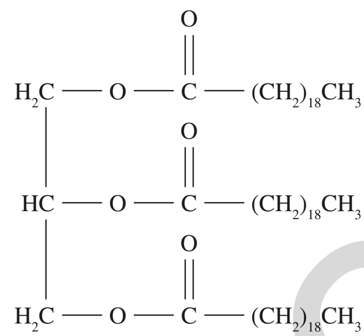


Thinking	**Working**
Identify the ester groups in the triglyceride.	
Split the molecule between each oxygen atom and the carbon in the fatty acid.	
Oxygen and hydrogen from sodium hydroxide must be introduced to produce glycerol and the carboxylate ion. A hydrogen atom is added to form glycerol. O is added to form the carboxylate ion.	Since sodium hydroxide was used, the metal ion is Na^+. 
Add the metal ion from the hydroxide used to produce the molecule of soap made. Sodium hydroxide was used. Note: In order to show the ionic nature of the bond between sodium and the ion of the fatty acid, charges are given in the structure.	Since sodium hydroxide was used, the metal ion is Na^+. 

Worked example: Try yourself 16.2.1

DETERMINING THE PRODUCTS OF SAPONIFICATION FROM A TRIGLYCERIDE

The following triglyceride was reacted with potassium hydroxide to form a soap. Give the products of this reaction.



LIMITATIONS OF SOAPS

In some parts of Australia, particularly Western Australia, soap has limited effectiveness. This is because the water supply in these regions contains high levels of metal ions such as Ca^{2+} and Mg^{2+}. Water containing significant concentrations of metal ions is described as **hard water**.

When a typical soap such as sodium stearate is added to hard water, the stearate ions mix with the calcium and magnesium ions. While sodium stearate is soluble, calcium and magnesium stearates are not and they precipitate from the wash as an unsightly scum. This reaction is illustrated by the equation:

$$2CH_3(CH_2)_{16}COONa(aq) + Ca^{2+}(aq) \rightarrow (CH_3(CH_2)_{16}COO)_2Ca(s) + 2Na^+(aq)$$

The net effect of using soap in hard water is:

- poorly washed clothes
- blocked drains from soap scum
- grey scum in wash tubs
- unsightly stains around basins and taps (Figure 16.2.8).

FIGURE 16.2.8 Lime scale around taps is caused by metal ions present in hard water.

CHEMFILE

Soap making—a way of life

The photo in Figure 16.2.7 shows how soap manufacturing is a way of life in Tripoli, in the north of Libya. A whole market is dedicated to the manufacture of soap and much of the produce is used in the nearby public baths.

This soap is made from oil extracted from the local olive trees. The olive oil is boiled in the cauldrons for 6 hours to ensure a smooth consistency and secret ingredients are added to ensure a unique product.

FIGURE 16.2.7 The manufacture of soap in Tripoli is part of the city's heritage. Families meet at a market and spend hours together cooking soap in large cauldrons.

To obtain a satisfactory result when washing with soap in hard water, either extra soap needs to be used to create an excess of fatty acid ions or some of the metal ions need to be removed. One indication of hard water is the failure of the soap to produce a lather.

Metal ions can be removed by adding other negative ions such as carbonate ions to the soap. The carbonate ions soften the water by precipitating the magnesium ions as magnesium carbonate. An equation for the precipitation of unwanted magnesium ions through the addition of sodium carbonate is:

$$Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MgCO_3(s)$$

DETERGENTS

During World Wars I and II, several countries such as Germany experienced severe shortages of fats or oils for soap making. Chemists looked for alternative ways to form substances with long non-polar chains and charged ends, and the result was the development of **detergents**. Detergents are cleaning agents that do not suffer from some of the drawbacks of soaps. As you can see in Figure 16.2.9, a long hydrocarbon chain is present in detergents, but this time it is sourced from petroleum products. The cleaning mechanism of a detergent is similar to that of soap because their structures contain the same features.

In contrast to soaps, detergents do not form insoluble salts with calcium ions or magnesium ions. For this reason, they proved a popular replacement for soaps in hard water areas and they are now widely used in many different cleaning products, including many hand washes and shampoos.

Anionic detergents

Most detergents, like most soaps, are anionic, such as the alkylbenzenesulfonate detergent (Figure 16.2.9). **Anionic detergents** are those whose active constituent is a negatively charged species. This can be composed of a sulfonate group attached to a long carbon chain, often via a benzene ring within the structure.

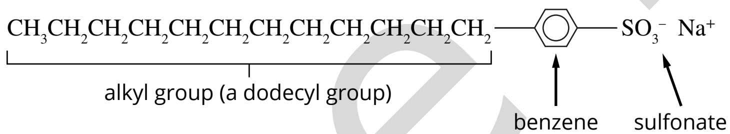


FIGURE 16.2.9 Structure of an alkylbenzenesulfonate detergent, sodium *p*-dodecylbenzenesulfonate.

Although the name of the detergent looks complex, it provides clues to the structure of the detergent.

- 'Alkyl' refers to the non-polar hydrocarbon chain.
- 'Dodecyl' means the hydrocarbon chain contains 12 carbon atoms.
- 'Benzene' is the hexagonally shaped aromatic hydrocarbon (sometimes called a phenyl group).
- 'Sulfonate' refers to the $–SO_3^-$ group, which makes a negatively charged end.

16.2 Review

SUMMARY

- Fats and oils are used to make soaps.
- Soap molecules contain a long, non-polar hydrocarbon section and a carboxylate group.
- Soaps are formed by a saponification reaction.
- Saponification is the base hydrolysis of a triglyceride to form glycerol and the salt of the fatty acid or acids present.
- Hard water is water containing significant concentrations of metal ions such as calcium and magnesium.
- Soaps form an insoluble salt with calcium and magnesium ions called ‘soap scum’ and make the cleaning action of soaps less effective.
- Detergents are made from petrochemicals and do not form insoluble salts with calcium and magnesium ions, making them more effective in hard water areas than soap.

KEY QUESTIONS

1 A hydrolysis reaction is one in which:
A water is a product of the reaction
B a soap is made as a product of the reaction
C a molecule is split apart by reaction with water
D water is removed from a substance.

2 Fill in the blanks for the following sentences.
The hydrolysis of a triglyceride can be achieved by using either __________ or __________ solutions. The reaction to make soap is called ______________________ and uses a base to catalyse the reaction. The soaps made are ____________ of the fatty acids that form the triglyceride. The other product from saponification is ____________________ .

3 What is meant by the term ‘hard water’?

4 What problems can hard water cause when using soap?

5 List as many similarities and differences as you can between soaps and detergents.

16.3 The cleaning action of soaps and detergents

The cleaning action of soap and detergent molecules can be explained by looking at their structure. Soap and detergent molecules are similar in structure and cleaning action, so the following explanation of the cleaning action of soap also applies to detergents.

SOAP IN WATER

In water, anions in soap tend to come together and form clumps. The **hydrophilic** ends are on the outer perimeter of these clumps where they will be in contact with the water. Hydrophilic means ‘water loving’ and typically refers to molecules or ions that can form strong forces of attraction with water. In the case of soaps, these forces of attraction are **ion–dipole forces**. Ion–dipole forces are produced between the ionic end of the soap, which carries charge, and the highly polarised O–H bond in water. The **hydrophobic** (non-polar) sections of the soap are in the centre of the clump where they are in contact with each other. Hydrophobic means ‘water hating’. This clump is a stable arrangement called a **micelle**. The sodium or potassium ions are spectator ions in the cleaning solution. A diagram of a micelle is shown in Figure 16.3.1.

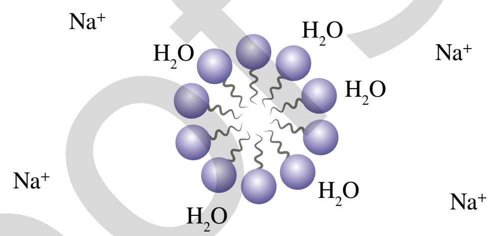


FIGURE 16.3.1 The arrangement of soap particles in a micelle. Micelles have a spherical shape.

CLEANING ACTION

During the washing of clothes, vigorous agitation is used to break up the micelles formed by soap. The non-polar ends of the soap particles are then able to position themselves in drops of oil or grease, leaving the hydrophilic ends exposed to the water. As the agitation continues, the water molecules are attracted to the polar ends of the soap and the oil particle is lifted from the fabric, as shown in Figure 16.3.2.

Once the oil lifts from the fabric, the non-polar sections of the soap embed themselves around the oil. The charged end of the soap protrudes into the water. The oil surrounded by soap molecules is a stable arrangement that prevents the stain reattaching to the fabric (Figure 16.3.3). When the water is drained from the wash, the oil stains are drained away as well.

The non-polar chain and charged end of soap particles enables them to function as cleaning agents. With the addition of soap, a polar solvent can successfully remove non-polar stains. The general term for substances such as soaps and detergents is **surfactant**, which is a shortened version of ‘surface active agent’. This process is the same whatever the surface happens to be: fabric, a ceramic plate, a glass bowl or skin.

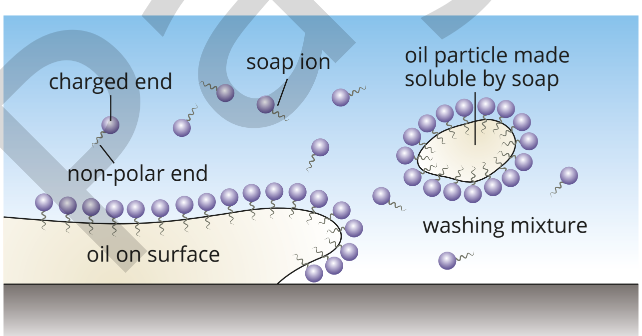


FIGURE 16.3.2 The cleaning action of soap. The non-polar chain of soap particles is embedded in an oil stain while the charged part is in the water.

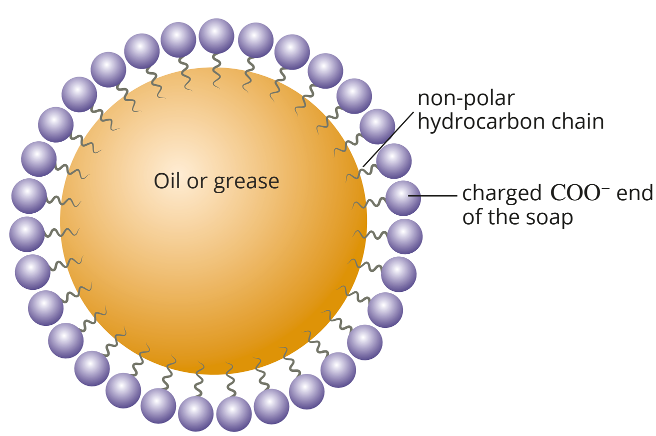


FIGURE 16.3.3 An oil or grease stain that has been lifted from the fabric

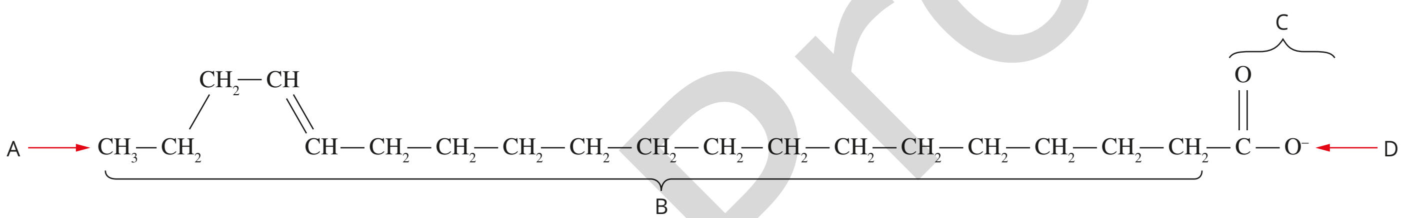
16.3 Review

SUMMARY

- The cleaning action of soaps and detergents is similar and can be explained by reference to their structure.
- There are two parts to the structure of soaps and detergents, which enable non-polar grease and oil to mix with water.
- Micelles form when a soap or detergent is dissolved in water.

KEY QUESTIONS

1 The structure shown corresponds to the anion of a soap molecule dissolved is water. Identify parts A–D by choosing from the following: hydrophilic, non-polar tail, hydrophobic, polar head.



2 Fill in the blanks for the following sentences. When enough soap is added to water, the anions of the soap molecule will form ___________________. Agitation breaks up these structures and allows the _______________ part of the molecule to dissolve in the oil or grease. As more soap dissolves in the oil, the stain lifts from the fabric helped by the attractive forces between the water and the ____________ end of the soap molecule.

3 Name the main intermolecular forces broken and formed when:

a a soap molecule dissolves in water

b a group of soap molecules form a micelle

c grease is removed from clothing.

16.4 Production of biodiesel

Biodiesel is a type of biofuel—a fuel that has been produced from plant or animal material (biomass). In this section, you will see how organic chemical reactions can be used to synthesise biodiesel.

THE NEED FOR BIODIESEL

The burning of **fossil fuels** is responsible for increases in the concentration of carbon dioxide in the atmosphere, and most scientists working in this field agree that that these changes are contributing to climate change. Fossil fuels are hydrocarbons geologically formed from the remains of living organisms. The increased use of biofuels is one approach to reducing carbon dioxide emissions.

Biodiesel is one of the most promising alternative fuels and its commercial use has increased over the last 20 years. In Australia, commercial biodiesel has been manufactured since 2006. Countries in Asia, including Indonesia, produce about 1.3 ML of biodiesel annually. Many Asian countries grow crops specifically to produce oils such as palm oil, which are then converted to biodiesel. Diesel containing 5% biodiesel has been available since 1995. All diesel-powered vehicles can run on 100% biodiesel. Biodiesel has some benefits compared to **petrodiesel**, which is a hydrocarbon fuel derived from crude oil. These benefits include improved engine wear and therefore engine lifespan.

Biodiesel is a mixture of organic compounds called esters. These esters are produced by a chemical reaction between vegetable oils or animal fats and an alcohol (most commonly methanol (CH_3OH)).

At present, far more petrodiesel than biodiesel is consumed, both locally and internationally (Figure 16.4.1). Petrodiesel is a **non-renewable** resource, meaning once used it is not replenished and amounts worldwide are depleted. Australia's total diesel consumption is over 23 000 ML/year. Biodiesel comprises only 400 ML of this total. This gap is likely to close in the future as the biodiesel industry is the subject of extensive scientific research.

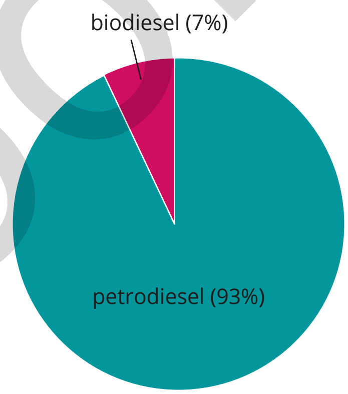


FIGURE 16.4.1 This pie chart shows world diesel consumption. Petrodiesel dominates world diesel consumption (2015 data).

TRANSESTERIFICATION

The structure of a typical biodiesel molecule is shown in Figure 16.4.2.

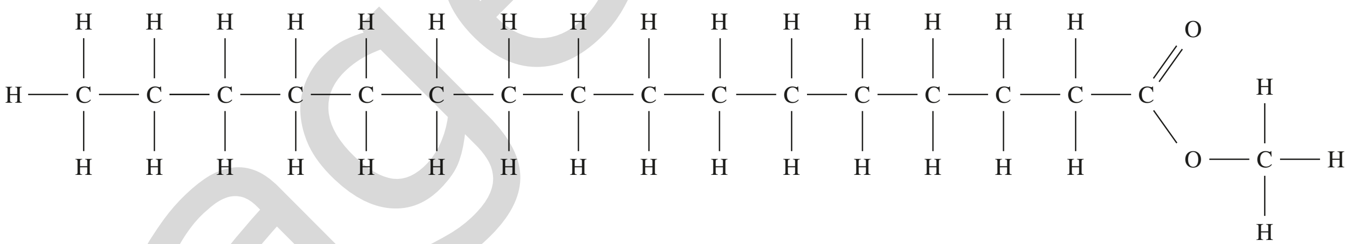


FIGURE 16.4.2 Structural formula of a typical biodiesel molecule

The usual raw material for the production of biodiesel is vegetable oil from sources such as soyabean, canola or palm oil. Recycled vegetable oil or animal fats can also be used.

The triglyceride is converted into biodiesel by warming it with an alcohol, usually methanol, in a process known as **transesterification**. The reaction requires a **catalyst**. A catalyst is a substance that provides an alternative reaction pathway that speeds up the rate of reaction and is not consumed in the reaction. The reaction can be carried out using a base, typically potassium hydroxide solution, or lipase, which is an enzyme, both of which catalyse the reaction. An **enzyme** is a protein produced by a living organism that functions as a catalyst.

In the transesterification reaction, the triglyceride is converted into glycerol and three ester molecules with long carbon chains. The ester molecules are the biodiesel product. The reaction is shown in Figure 16.4.3.

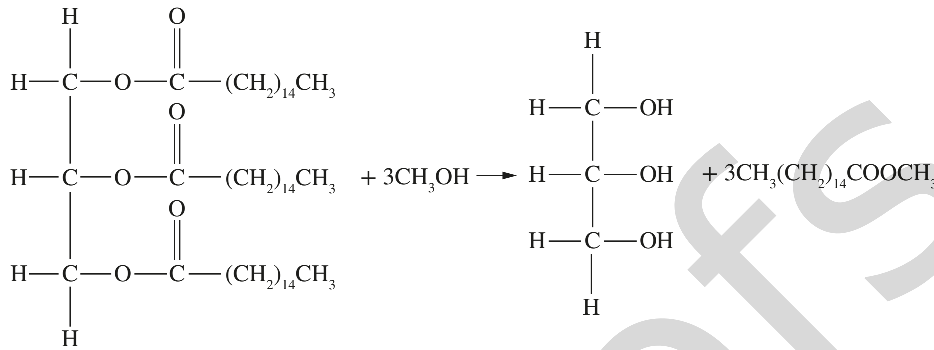


FIGURE 16.4.3 The reaction of a triglyceride with alcohol to form fatty acid esters (biodiesel) and glycerol

The structure of a typical biodiesel molecule is shown in Figure 16.4.2. Molecules of this type are sometimes referred to as **fatty acid esters**, because carboxylic acids with relatively long hydrocarbon chains are referred to as fatty acids. A fatty acid ester is an ester made from a fatty acid and simple alcohol.

Like petrodiesel, biodiesel is not a pure substance. The structure of the triglyceride varies depending on the particular plant or animal used as the source. Triglycerides produced by animals, such as tallow, usually form saturated esters, which have only carbon–carbon single bonds in the hydrocarbon chain. However, triglycerides produced by plants often form unsaturated esters like the one shown in Figure 16.4.4.

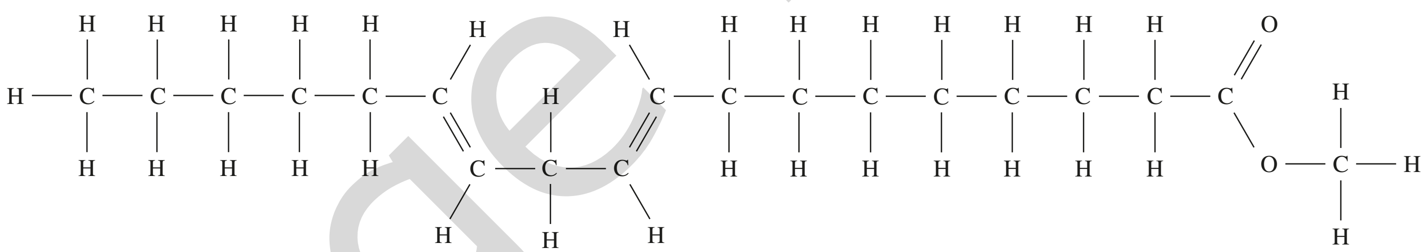


FIGURE 16.4.4 Biodiesel molecules derived from plants often contain carbon–carbon double bonds.

The term 'saturated' refers to hydrocarbons that contain only single bonds between the carbon atoms. They are said to be saturated because each carbon atom is bonded to as many hydrogen atoms as possible. 'Unsaturated' means that there is at least one carbon–carbon double or triple bond within the hydrocarbon chain.

MANUFACTURING BIODIESEL

In the production of biodiesel, the triglycerides (usually an oil), methanol and a catalyst are added to a reactor in a batch process. The initial mixture is heated gently and left for at least 30 minutes; the time depends on the catalyst used and conditions selected. The reaction mixture is then pumped to a separator as shown in Figure 16.4.5.

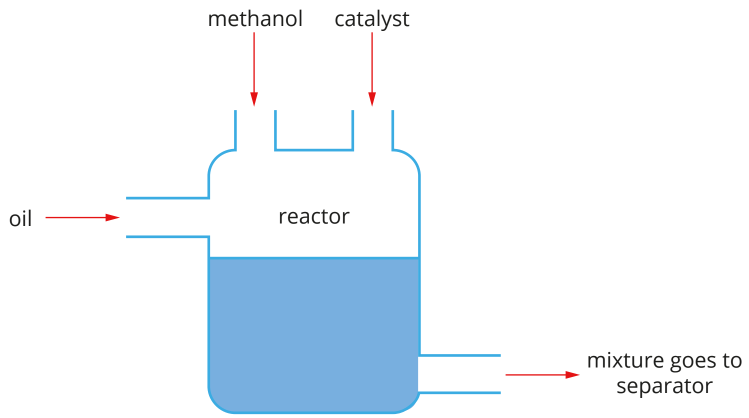


FIGURE 16.4.5 A flow chart of the first step in the production of biodiesel

One of the products, glycerol, is a relatively small molecule with three hydroxyl functional groups and is quite polar. Conversely, the long hydrocarbon chain on the methyl ester makes the molecule non-polar. This means that in the separator, the two products do not dissolve in each other and separate into two distinct layers, like the oil and water shown in Figure 16.4.6.

The biodiesel and glycerol extracted from the separator are then distilled to remove any unreacted methanol, which is recycled back into the reactor. The biodiesel and glycerol can then be collected separately as shown in Figure 16.4.7.

FIGURE 16.4.6 A mixture of paraffin oil (coloured blue) and water (clear) separates into two distinct layers. In a similar way, biodiesel and glycerol are separated in the separator during the production of biodiesel.

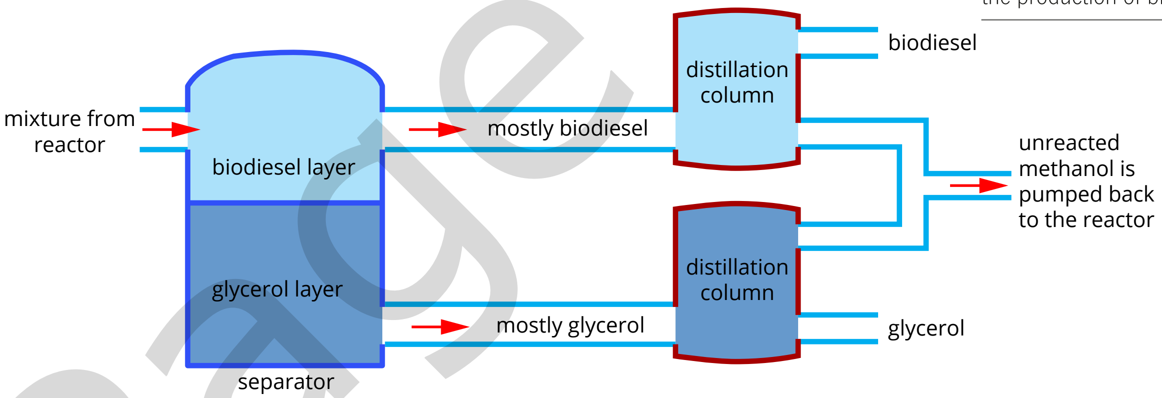


FIGURE 16.4.7 The separation of products of the transesterification process during the manufacture of biodiesel

The glycerol produced from this process is about 80% pure. Increased biodiesel production has resulted in an oversupply of glycerol to the market, leading to a fall in the price of glycerol. Finding uses for the excess glycerol would increase the economic viability of the biodiesel industry.

Choosing a catalyst

Two types of catalysts can be used in the production of biodiesel: the lipase enzyme, a naturally occurring enzyme (Figure 16.4.8); and a base, generally sodium hydroxide or potassium hydroxide.

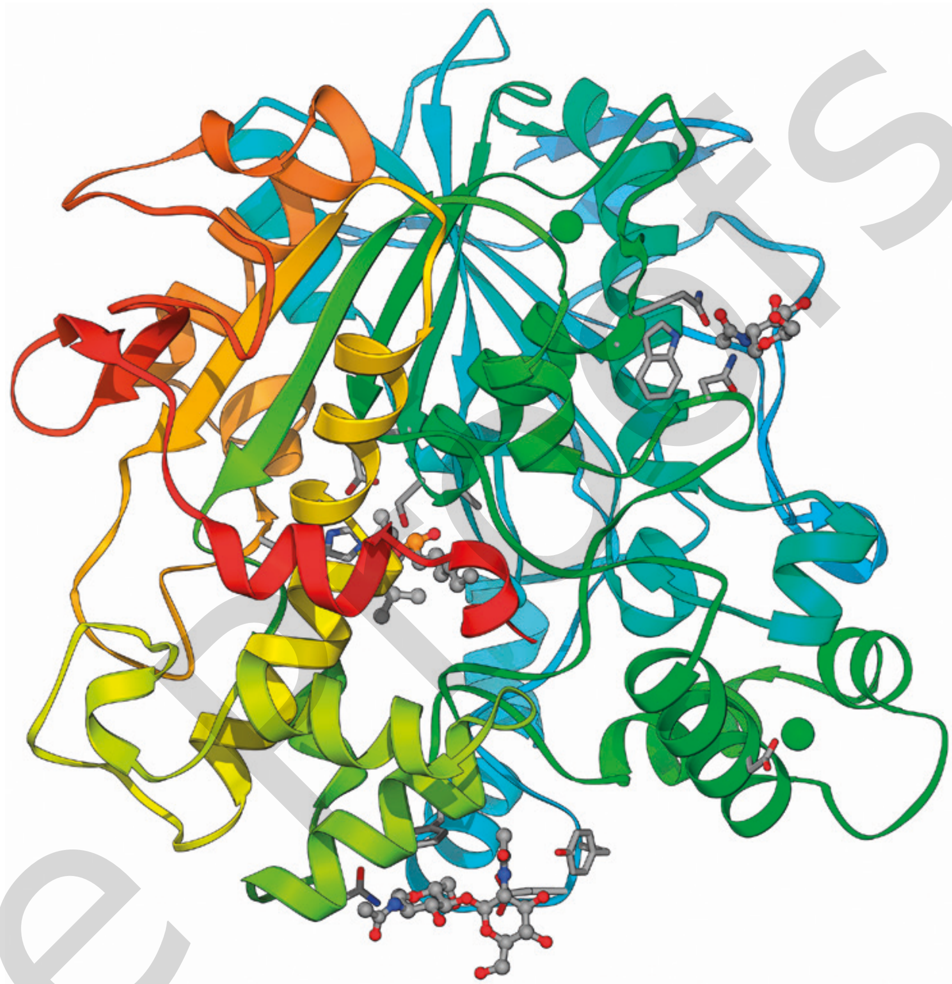


FIGURE 16.4.8 The structure of a lipase enzyme molecule. The lipase molecule is a large protein made up of many spiralled (alpha helix) structures.

At present, the base-catalysed process is used in almost all biodiesel plants. Unlike the lipase-catalysed production of biodiesel, the base-catalysed process can use methanol and operate at high temperatures, making the conversion process quicker and more economical. Using lipase instead of a base would be preferable because lipase can be used many times, while the base can only be used in one batch. Lipase also requires less energy to produce biodiesel and the transesterification process can be carried out at lower temperatures and pressures, which can reduce costs.

Unfortunately, the slow rate of reaction using naturally occurring lipase limits its use. Industry is researching possible ways of increasing the rate of the reaction using lipase, such as:

- chemical modification of the enzyme
- protein (genetic) engineering
- using organic solvents.

Table 16.4.1 summarises the differences in the two alternative methods for catalysing the production of biodiesel.

TABLE 16.4.1 Comparison of the operating conditions for base-catalysed and lipase-catalysed production of biodiesel

Method	Temperature (°C)	Pressure (kPa)	Time (min) in reactor	Catalyst use	Yield (%)
Base-catalysed	60–70	140–400	30–60	Only able to be used for one cycle of the production process	96–98
Lipase-catalysed	20–37	101.3	at least 150	Can be used many times	Typically 80 (can be as high as 92)

In the base-catalysed production of biodiesel, the amount of base added must be carefully monitored. When a mole ratio close to 3:1 of base to triglyceride is reached, soaps can form. Not only does soap formation reduce the conversion of triglycerides to biodiesel, it can also affect the separation process.

Green chemistry

Green chemistry is a set of 12 principles to guide chemists in producing environmentally sound products and processes. These principles demonstrate the breadth of the concept of green chemistry.

The 12 principles of green chemistry are:

1. prevent waste
2. maximise atom economy
3. design less hazardous chemical syntheses
4. design safer chemicals and products
5. use safer solvents and reaction conditions
6. increase energy efficiency
7. use renewable raw materials
8. avoid chemical derivatives
9. use catalysts, not excess reactants
10. design chemicals and products that are biodegradable
11. analyse in real time to prevent pollution
12. minimise the potential for accidents.

These principles are explained in more detail in Chapter 12.

The continued research and development of the lipase-catalysed reaction for the production of biodiesel focuses heavily on employing some of these principles. Optimising the process with these principles would make the reaction more environmentally acceptable and also economically attractive.

Wider environmental considerations

The burning of biodiesel and petrodiesel produces carbon dioxide, a greenhouse gas. In the case of biodiesel, carbon dioxide is absorbed from the atmosphere in the growth of the plant or animal the biodiesel is derived from, reducing the net impact on greenhouse gas levels.

In Australia, waste oil is commonly used as a feedstock for the production of biodiesel (principle 7). Elsewhere, such as parts of Asia, crops are grown for the sole purpose of producing biodiesel. This requires massive land clearance, which destroys natural habitats. The intensive farming methods used require water and fertiliser. Additionally, farm machinery emits carbon dioxide and offsets a benefit of using biodiesel. These factors clearly increase the environmental impact of biodiesel, albeit indirectly.

The use of either form of diesel produces pollutants such as nitrogen oxides, carbon monoxide and unburnt fuel. Petrodiesel also produces some sulfur dioxide (SO_2) emissions. Whether biodiesel produces SO_2 depends upon the origins of the triglycerides that it is produced from. For example, soyabean oil does not contain sulfur but canola oil does. Biodiesel exhaust contains up to 20% less particulate matter than diesel.

CHEMISTRY IN ACTION

Biodiesel in Western Australia

Bioworks is a company based in Henderson in Western Australia. Currently, Bioworks produces 4 ML (4 000 000 L) of biodiesel per year and is expanding this production to 6 ML. Businesses around the state are paid for their waste oils from cooking and food preparation, which Bioworks processes into biodiesel.

The oils collected and used contain very little sulfur (<0.001%) compared to petrodiesel and so reduce atmospheric sulfur dioxide pollution. As the oils and fats are collected from local sources, the emissions associated with collection are minimised, making the process more attractive from a green chemistry perspective.

Jonathon Thwaites is a sustainability expert who has run his vehicle on biodiesel since 2006. He makes the biodiesel himself in his shed. His equipment includes a 200 L drum, which acts as the reactor vessel. Jonathon performs a titration to determine the amounts of base and methanol he must add. His cost of production is around 30 cents per litre, excluding his time. To make his biodiesel, Jonathon had to obtain licenses from his local council and must pay fuel tax to the Australian Taxation Office, which significantly increases the final cost of the biodiesel.

The initial investment in equipment coupled with the time to learn the process, the cost of tax and licensing and the varying price of petrodiesel may make the potential financial saving of producing biodiesel unattractive to most people.

FIGURE 16.4.9 Jonathan Thwaites runs his vehicle on biodiesel made from waste oil in his backyard shed.

16.4 Review

SUMMARY

- There is a need to seek sustainable alternatives to fossil fuels for a number of reasons, including climate change and the increasing consumption of non-renewable energy sources.
- Biodiesel is a mixture of methyl fatty acid esters produced from a transesterification reaction.
- Transesterification involves the reactions of a triglyceride containing three ester groups with methanol to produce three methyl ester molecules and glycerol.
- The industrial manufacture of biodiesel is normally carried out using a base-catalysed reaction.
- Research continues to improve the use of lipase to catalyse a synthesis that employs green chemistry principles.

KEY QUESTIONS

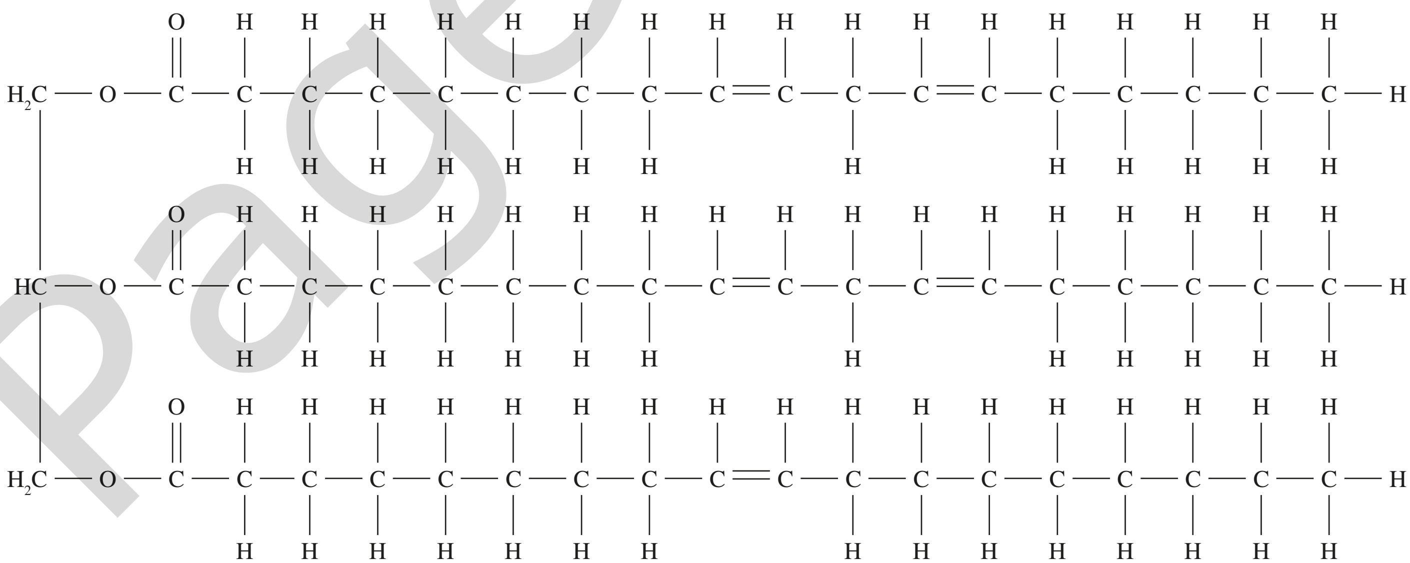
1 What is the name of the reaction in which a triglyceride is broken down to form biodiesel molecules?

2 Determine if the following statements about biodiesel are true or false.
  - **a** Biodiesel can contain several different compounds.
  - **b** Biodiesel molecules contain ester groups.
  - **c** Biodiesel is an alkane.
  - **d** Three molecules of biodiesel can be obtained from each molecule of a triglyceride.
  - **e** All hydrocarbon chains in biodiesel molecules are saturated.
  - **f** Biodiesel is formed in a transesterification reaction.

3 Why are the CO_2 emissions from the use of biodiesel not considered as problematic as those produced from petrodiesel?

4 What are the advantages and disadvantages of the lipase-catalysed reaction compared to the base-catalysed manufacture of biodiesel?

5 Write an equation showing the reaction of the following triglyceride to produce biodiesel.



Chapter review

16

KEY TERMS

anionic detergent
base hydrolysis
biodiesel
carboxylate
catalyst
detergent
enzyme
ester functional group
ester link
fatty acid
fatty acid ester
fossil fuel
green chemistry
hard water
hydrolysis
hydrophilic
hydrophobic
ion–dipole force
lipid
micelle
monounsaturated fatty acid
non-polar
non-renewable
petrodiesel
polar
polyunsaturated fatty acid
saponification
saturated
saturated fatty acid
soap
surfactant
transesterification
triglyceride
unsaturated

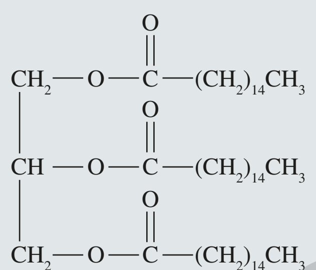
Fats and oils

1 Which two functional groups are directly involved in the formation of a triglyceride?

2 a Write an equation for the formation of the triglyceride glyceryl trioleate from the reaction of glycerol and oleic acid ($CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$).

b Draw the structure of the glyceryl trioleate, showing the ester bonds.

3 A fat present in vegetable oil has the structure shown.



a Circle an ester functional group.

b Is this triglyceride saturated or unsaturated? Explain your answer.

Production of soaps

4 Which one of the following is the formula of a soap?

A $CH_3(CH_2)_{16}COOH$

B $CH_3(CH_2)_7CHCH(CH_2)_7COOLi$

C CH_3COONa

D $CH_3(CH_2)_{16}COOCH_3$

5 If 0.2 mol of a triglyceride undergoes saponification completely in excess base, determine the number of moles of:

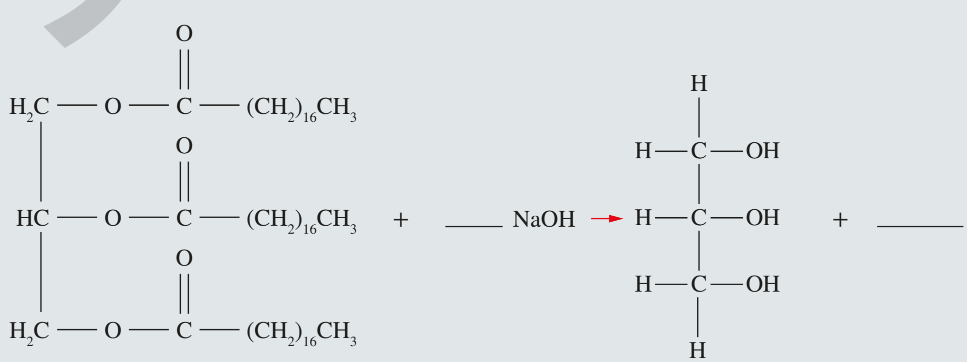
a sodium hydroxide required for the reaction

b glycerol formed.

6 Complete the summary about saponification by using some of the following terms: carboxylate, acid, positive, hydrocarbon, triglyceride, ester, fatty, hydroxyl.

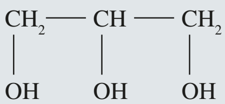
When a ________________ undergoes saponification, a ____________ ____________ salt is formed. Particles of this substance have a long _____________ chain, a _______________ group and a _______________ metal ion.

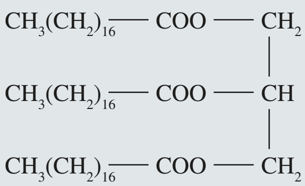
7 Copy and complete the equation showing the formation of soap in the reaction of the following fat with sodium hydroxide solution.

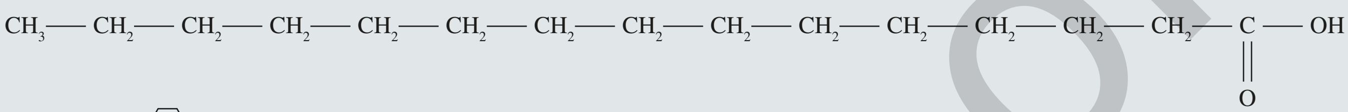


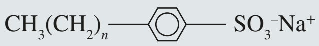
The cleaning action of soaps and detergents

8 Identify each of the following as a detergent, a soap, a fatty acid, a fat or glycerol.

a 

b 

c 

d 

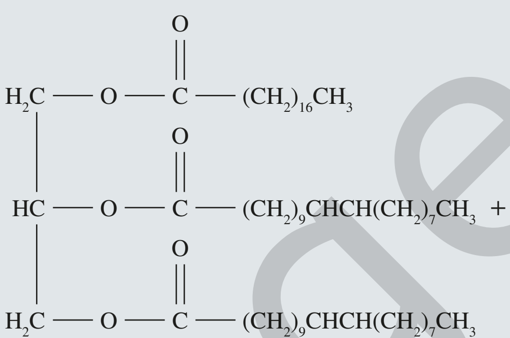
e $CH_3(CH_2)_{16}$— COO^-Na^+

9 Both saturated and unsaturated fats can be used to make soap. What differences would you expect between a soap made with a saturated fat and a soap made with unsaturated fat?

Production of biodiesel

10 Briefly explain the need for biodiesel.

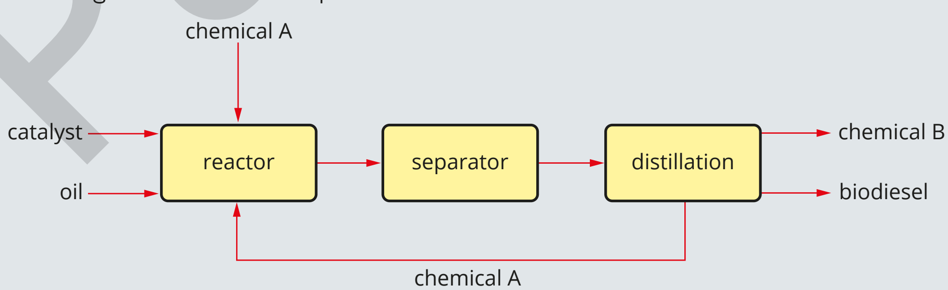
11 Complete a balanced transesterification reaction for the following triglyceride.



12 What does the term 'renewable feedstock' mean?

13 The transesterification reaction to make biodiesel requires the use of a catalyst. What is a catalyst?

14 Use the diagram to identify the chemicals used in the following transesterification process.



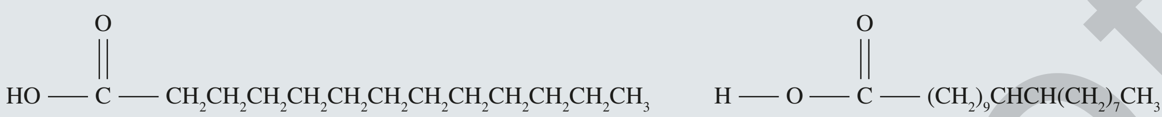
a Name chemical A.

b Name chemical B.

15 Transesterification is a reversible reaction. Usually, about twice the stoichiometric amount of methanol is added in the base-catalysed reaction to make biodiesel. Using your knowledge of equilibrium, explain why this is done.

Connecting the main ideas

16 Select one or more of the following molecules that match the following descriptions.



a A triglyceride likely to be from an animal source

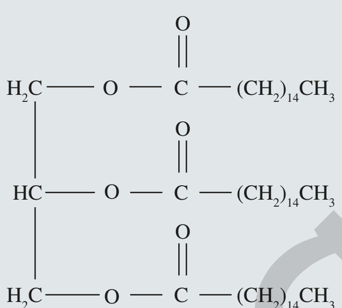
b An unsaturated triglyceride

c A soap molecule made from the triglyceride in part **a**

d The biodiesel formed when part **b** undergoes transesterification

17 Suggest why, when adding a base to the triglyceride when making biodiesel, you should take care to ensure that the base-to-triglyceride stoichiometric ratio should not approach 3:1.

18 Compare and contrast saponification and transesterification reactions using palm oil to illustrate your answer.



palm oil