**CHAPTER**

From fats and oils to soaps and biodiesel

P The large obtained Fats from encountered have economics inform At soaps molecule(s) You reaction disadvantages Science • Science • • • Chemistry Scientific pathways, environmental and Chemical construction involves optimise The the The carboxylate dodecylbenzene the a will industrial and to fats amounts salt base structure and biodiesel end choices consider also in oils ATAR from and of the detergents of base-catalysed the and knowledge hydrolysis synthesis produced a taking learn as understanding are already. Course this oils group; long production selection naturally of of g of rate around profitability. of one impacts issues a each raw reaction chapter, makes about soaps extracts contains into chain and human such the When materials. to clean (saponification) from process can the account of such yield occurring form © the contains structure use fatty (green of sequences you particular School feedstock. and conditions be e the a a and The many manufacture as of of given non-polar products acid used will enzyme-catalysed will endeavour processes Curriculum the organic sustainability These sustainability, principles how chemistry), a sources. be of chemical be (soap) fat product to non-polar reagents The the to with able and highlighted. design of raw or with determine reactions, hydrocarbon and fats anionic oil. production of are more reagents to materials, of Standards specific including substances biodiesel describe (triglycerides) green alternative and and used hydrocarbon P local than detergents processes. some reaction the the Authority on resources, chemistry used properties of called one chain environment and the how an structure soap requires of chemical in chemical industrial production (2017); r the which conditions soaps produces chain the and feedstocks, derived The and can economics transesterification may processes. reproduced a of the advantages you are biodiesel and sulfonate synthesis be o the reaction alongside scale, require from use made, glycerol of will used in a soap are ethanol order by of have

and scientists

permission. to often

group the how

and

and

and to o

**434**

AREA OF STUDY 6 | ORGANIC SYNTHESIS: HOW DO CHEMISTS BUILD MOLECULES?

**16.1 Fats and oils**

H

H

C C

C

H glycerol SOURCES ‘Fat’ larger types are fats the liquids one STRUCTURE Fats polar similar physical • • fats General Triglycerides and or with functional tail carbon OH more Fats Olive fats oils Being also carbon–carbon makes tend and or three and three is of molecules e class more at are are atoms, a chemical members and carbons lipids. oils state to oil, name non-polar, oils room fatty hydroxyl group up liquids. solids exist of structure oils are double canola are at contain the OF biological usually Compounds temperature. used O insoluble acids. room as have are atoms. synthesised attached structures of OF bulk FATS solids bonds functional or typically oil triglycerides the to no large temperature. between FATS triple Fatty of and Glycerol describe lipid molecules at P overall in are the AND of to room non-polar such palm water. carbon–carbon by Plant and acids obtained family. a single molecule. AND a groups eight long condensation dipole (propane-1,2,3-triol) fatty a as temperature. are OILS oil are oils are number At called waxes bonds. unbranched and unable r are OILS distinguished (Figure room from carboxylic are present molecules Most acid 20 common lipids. and mainly of to (Figure either bonds. temperature: reactions o They fatty form 16.1.1). organic steroids in and hydrocarbon Fats acids unsaturated the plant plant known acids are hydrogen 16.1.1). simply glycerol molecule. and is between compounds (which Fatty with mainly or a oils. o have relatively as oils animal on chain They acids triglycerides. bonds include chain, saturated an are a fats—they Fats the glycerol even sources. have lengths the usually small belonging basis with and or f cholesterol) best-known

number a ‘tail’. molecule molecule oils water, carboxyl fats—all

of of contain exist Animal s

Non-

eight

This have their to so as

of a

OH

OH

fatty acid (stearic acid) HO C CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

3

**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.

H

H

2

O is formed

O

H

C OH

HO C H

C

OH

(CH

2

H

C

OH

H

H

H

H

ester link

+ o 3H

2

H

glycerol fatty acids triglyceride

**FIGURE 16.1.2**

O

(CH

2

)

16

CH

3

HO

C O

)

16

CH

3

HO C

(CH

2

)

16

CH

3

The reaction between glycerol and fatty In the example in Figure 16.1.2, the three but triglycerides can often have two or three that carbon–carbon SATURATED different chains acids produces on fatty the a triglyceride acid triglyceride hydrocarbon P and are water.

identical, r chains

o

Fats their • • • can differ in length. Some double bonds. AND UNSATURATED are classified according fatty acid components. Saturated fatty acids have carbon bonds. Stearic formula Monounsaturated in which CH Polyunsaturated in polyunsaturated structural their 3 their (CH P is hydrocarbon of 2

) hydrocarbon formula found 7 CH

CH=CH(CH

3

(CH fatty fatty a in CH fatty 2 chain. ) a acids. acids 16

3 acid, to hydrocarbon the hydrocarbon g which structural occurs chains chains features e

FATTY widely that may of contain in the ACIDS

also meats, hydrocarbon contain only has single one a or more chains of

carbon– structural COOH. acids contain chain. The number of one carbon–carbon double bond main dietary example is oleic acid, vegetable oils. Its structural formula is

2

)

7

COOH. contain more than one carbon–carbon double bond Fish and vegetable oils are the main dietary source of Linoleic acid, which occurs in sunflower oil, has the (CH

2

)

4

CH=CHCH

2

CH=CH(CH

2

)

7

COOH.

435 CHAPTER 16 | FROM FATS AND OILS TO SOAPS AND BIODIESEL

O

C O

C (CH

2

(CH

2

CH )

16

3

O

O

C O

O

C (CH

2 C

)

16

CH

3 O C

H

)

16

CH

3

f

s

**436**

AREA OF STUDY 6 | ORGANIC SYNTHESIS: HOW DO CHEMISTS BUILD MOLECULES?

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

**saturated fatty acid**

H

3

stearic acid C

17

**monounsaturated fatty acid polyunsaturated fatty acid**

O

O

C(CH

2

)

16

C

H

3

C(CH

2

)

7

CH CH(CH

2

)

7

C

OH

OH

**FIGURE 16.1.3**

oleic acid C

17

H

3

C(CH

2

)

4

CH CHCH

2 CH o CH(CH f 2

)

7

C s O

OH

linoleic acid H

35

COOH

H

33

COOH

C

17

H

31

COOH

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

P

a

g USES Fats and and for substances. predominant manufacturing in and TABLE End Paints Inks Candles Pharmaceuticals, Thermoplastics Cosmetics, Soap Biodiesel vehicle The cooking. related oils oils and use 16.1.1 e will OF may other oils engines e.g. Non-food industries. Table be FATS have be non-food 25% lipstick biodiesel explored used e.g. a and 16.1.1 uses wide of pill AND directly Globally, is global formulations of uses further made variety P shows fats (approximately OILS and by in production from this of in food, oils some volume uses, the accounts fats r as remainder other but and an Oil Soybean Soybean Hydrogenated Various Linseed Olive Tallow, Palm, are 20%). is the ingredient, used for o uses in majority about the as for production a 75% oil raw for of and applications frying of material production. fats. of food Note soap to or are make as The that and in a food new fuel fats

the for Biodiesel is a fuel that can be used oils. These two important uses of fats

of this chapter.

**or fat used**

oil

oil

vegetable oils

vegetable oils

oil, cocoa butter

olive oil, palm oil and others

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.

KEY QUESTIONS

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

**a**

H

2

• 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.

P

2 3 For each ester groups Draw the Question of 1a.

two the in molecules structures each o molecule.

that in Question o form the 1, identify f

s

the

fat given in

H

C

H

H

H

H

H

H

H

H

H O

C O

C (CH

2

)

14

CH

3 O

HC

O C (CH

2

)

14

CH

3 O

H

2 C b

H H H

H O C (CH

2

)

14

CH

3

H

H

C C H

C e C P

H H H

H

H

C C C H

H

H r

H

H

C

C C C C C C C C H

H

H

H

HC

O CO a H

H C

H

C

H

g H

H C H

H

H

H

H H H

H H H

H

H

H

H

C C C C C C C C C C C C C C H

H

H

H

H

H

H

H

H

H

C O

H

2

C

CO H

O

H

H

H

H

H

H

H

H H H

H H H

H

H

H

H

H

2

C

CO C

C

C C C C C C C C C C C C C C H

H

H

H

H

H

H

H

H

HHH

H

H

H

H

437 CHAPTER 16 | FROM FATS AND OILS TO SOAPS AND BIODIESEL

**438**

AREA OF STUDY 6 | ORGANIC SYNTHESIS: HOW DO CHEMISTS BUILD MOLECULES?

P

a

**16.2 Production of soaps**

g

In constituents, with and the process SAPONIFICATION Soap structure FIGURE theory, down with hydroxide base saponification FIGURE the To CH CH Na+

CH alcohol that three water hydrolysis. molecules 2

**2 e a 16.2.1**

16.2.2 previous synthesise –O water of compound hydrolysis of manufacturing is −OH CO

CO

CO is that sodium The namely used. can O C very formula form section, contain (Figure groups). O O be When soap slow, The CH with used stearate, are fatty the 2

(CH

(CH CH of from reaction known so a strong 16.2.2). you sodium base P acids for 2 ester. In 2

2 soaps CH long )

)

16

16 a CH

CH this Chapter a 2 were strong CH a hydrolysis (long common stearate, 3

3 hydrocarbon This bases as triglyceride, from 2 with reaction. CH introduced hydrolysis 2 chain base CH knowledge r will oils. 14 water a 2 soap, CH typical is you produce such Reactions carboxylic applied 2 CH under chain the o learnt is soap to 2 as CH reactions. shown is ester triglycerides sodium 2 important a CH alkaline attached specifically how in salt acids) 2 CH which bonds in of esters 2 o In Figure CH hydroxide the and conditions to 2 practice, water in CH must (triesters) to carboxylic a glycerol can understanding 2 charged 16.2.1.

CH be 2 CH f hydrolysed, (an 2 CH and end. acid 2 alcohol

CH s their

The

3 and the

be broken. In is used to break the reaction or potassium is known as esters, it is called

CH

2

OH –OOC(CH

2

)

16

CH

3

CH

OH +

–OOC(CH

2

)

16

CH

3 O

+ 3OH–

(CH

2

)

16

CH

3

CH

2

OH

–OOC(CH

2

)

16

CH

3 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.

CH

2

fatty acid anion

metal cation

O

K+

–O

C carboxylate group long hydrocarbon chain

**FIGURE 16.2.3**

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

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 coloured spheres for atoms (white Even if a pure source vary. For this reason, in represent the fatty acid Figure 16.2.5.

O

representation the hydrocarbon of for general oil hydrogen, is used, of equation the black groups structure the for fatty carbon for as of saponification, a acids R, and fatty red acid for anion oxygen).

in a soap uses

r

CH

2

O

C R O

R′ in and the P

R′′, triglyceride chemists as shown often can

in

CH

CO

R

CO

R

triglyceride glycerol fatty acid ions

**FIGURE 16.2.5**

3OH–

e CH

CH CH 2

2

OH

RCOO–

CH

2

O

hydrocarbon SOAP Soap region. Europe. oil which may that process with Soap used then manufacturers removes Palm concentrated is PRODUCTION can P by be one groups. General small be dried oil where most made is popular soap and equation a reactants of usually sodium in moulded manufacturers the a school in for glycerol Asian select hydrolysis hydroxide + are to g laboratory placed countries shape. a and triglyceride of who solution. a any in triglyceride. The use by a and residual vessel, heating laboratory a OH +

R COO–

OH

R COO–

R, R′ and R′′ represent different

that is readily olive oil is widely a mixture The product is sodium hydroxide. process traditional batch the reaction available in their used in southern

of a suitable fat or rinsed with water, The soap is very similar to process. A batch takes place over a period of time and then the products are removed.

439 CHAPTER 16 | FROM FATS AND OILS TO SOAPS AND BIODIESEL

o

o

f

s

**440**

s

The reaction.

following triglyceride a

was reacted g

with retain out of Worked DETERMINING sodium gums A to by-product e

it use in and hydroxide example for the A resins, other soap soap THE of production to purposes. to paints, soap 16.2.1 PRODUCTS form improve P manufacture a explosives assembly soap, Glycerol the OF sodium moisturising line. SAPONIFICATION r and is is glycerol. a laxatives. laurate. common o properties, Some Give ingredient FROM the soap o products while manufacturers A f like to others separate it in the manufacture P

H

2

**TRIGLYCERIDE**

of this

O

C O

C (CH

2

)

11

CH

3 O

HC

O C (CH

2

)

11

CH

3 O

H

2

C O C (CH

2

)

11

CH

3

AREA OF STUDY 6 | ORGANIC SYNTHESIS: HOW DO CHEMISTS BUILD MOLECULES?

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**

**Thinking Working**

Identify the ester groups in the triglyceride.

H

2

C O

CH

3

H

2 HC

O C (CH

2

)

11

CH

3 O

Split the molecule between each oxygen atom and the carbon in the fatty acid.

H

2

o

CH C O C (CH

2

)

11

3

O

H

2

C HC P H

2 C O

C O O r O

O C C o (CH

(CH

(CH

2

2

2

)

)

11

11

CH

CH

CH

3

3

3

O

O

CH

3

Oxygen and hydrogen from sodium hydroxide must be introduced to produce glycerol the carboxylate ion. A hydrogen atom is

and

e

C (CH

2

CH

3

added to form glycerol. O is added to form the carboxylate ion.

C O

C (CH

2

)

11 H

2

C (CH

2 HC O

C O

O a

g

Since sodium hydroxide H

2

C OH

3 –O

H

2

)

11

CH

3

was used, the metal ion is Na+.

O

HC C (CH

2

)

11

CH

3 Add produce hydroxide Note: bond acid, the charges between In P metal order the was molecule are to ion sodium used.

show given from of and the in the soap the ionic the hydroxide structure.

made. ion nature of used to Sodium

of the the fatty

OH +

C OH

Since sodium hydroxide was used, the metal ion is Na+.

H

2

C OH

Na+ –O

H

2

O

HC OH +

3

C (CH

2

)

11

CH

3

C OH

441 CHAPTER 16 | FROM FATS AND OILS TO SOAPS AND BIODIESEL

O

C (CH

2 O

)

11

)

11

)

11

f

s

**442**

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 used This from is to secret a FIGURE unique boiled soap ensure soap the in ingredients 16.2.7 the and in local product. is a the nearby smooth made much P The olive cauldrons manufacture are from of public trees. consistency the added oil produce for baths. a The extracted 6 to of olive hours ensure and soap is oil

in g

Tripoli is part of the city’s heritage. Families meet at a market and spend hours together cooking soap in large cauldrons.

AREA OF STUDY 6 | ORGANIC SYNTHESIS: HOW DO CHEMISTS BUILD MOLECULES?

**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.

H

2

O

C O

C (CH

2

)

18

CH

3 O

HC

O C (CH

2

)

18

CH

3 O

H

2

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 Ca2+ and Mg2+. 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

C O C (CH

2

)

18

CH

3

(CH

2

)

16

COONa(aq) + Ca2+(aq) → (CH

3

(CH

2

)

16

COO)

2

Ca(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**

e

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

P

r

o

o

f

s

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:

Mg2+(aq) + CO

3

2−(aq) → 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 petroleum soap magnesium hard including Anionic Most detergent is to a a In negatively long water hydrocarbon because contrast detergents, carbon many (Figure products. areas detergents

ions. their charged to hand and chain, soaps, For like 16.2.9). chain structures The they washes this most species. often detergents is are cleaning reason, Anionic present soaps, via and contain now This a shampoos.

they widely benzene do are mechanism in can detergents the not detergents, proved anionic, be same used form composed ring in features.

a of insoluble within such are popular many but a those detergent as of this the different a the salts replacement sulfonate whose structure.

time alkylbenzenesulfonate with is P it cleaning active similar is calcium group sourced for constituent to products,

attached soaps ions that r from

or of

in

alkyl group (a dodecyl group)

benzene sulfonate FIGURE structure CH 3

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH e 2

CH

2

SO

3

– Na+

**• • • 16.2.9**

Structure of an alkylbenzenesulfonate g

detergent, sodium p-dodecylbenzenesulfonate.

• Although ‘Alkyl’ ‘Dodecyl’ ‘Benzene’ phenyl ‘Sulfonate’ P of refers group). the means is the refers the detergent. to name the hexagonally the to a non-polar the hydrocarbon of −SO

the detergent looks complex, it provides clues to the

hydrocarbon chain.

chain contains 12 carbon atoms. shaped aromatic hydrocarbon (sometimes called a

3

− group, which makes a negatively charged end.

443 CHAPTER 16 | FROM FATS AND OILS TO SOAPS AND BIODIESEL

o

o

f

s

**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.

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 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ .

P

a

g

e

3 4 5 • • P What What soap? List between Soaps magnesium cleaning Detergents do magnesium hard as not is problems water many meant form form soaps action r areas are similarities an ions ions, insoluble by and can made insoluble of the called than making soaps detergents. hard o term from salts soap. and ‘soap water less salt them ‘hard petrochemicals with differences with effective. scum’ cause o more water’? calcium calcium and when effective as and make you and using and f in

can the

**444**

AREA OF STUDY 6 | ORGANIC SYNTHESIS: HOW DO CHEMISTS BUILD MOLECULES?

s

**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.

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.

O

H

2

O

H

2

O

**FIGURE 16.3.1**

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

oil on surface

oil particle made charged end

soluble by soap

washing mixture

**FIGURE 16.3.2**

non-polar P end

a soap ion

g

e

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.

445 CHAPTER 16 | FROM FATS AND OILS TO SOAPS AND BIODIESEL

P

non-polar hydrocarbon chain

Oil or grease

**FIGURE 16.3.3**

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

r

Na+ o Na+

f o H

2

O

H

2

O

charged COO− end of the soap

s Na+ H

2

Na+

**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.

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.

• Micelles form when a soap or detergent is dissolved in water.

P

o

f

CH

2 CH CH

3

CH

2

CH CH

2

CH

2

CH

2

CH

2

CH

2

B

CH

2 P CH

2

CH

2 r CH

2

o

CH

2

C

O

CH

2

CH

2

CH

2

C O–

A

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.

e

g

a

**446**

AREA OF STUDY 6 | ORGANIC SYNTHESIS: HOW DO CHEMISTS BUILD MOLECULES?

s

D

**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. 5% biodiesel has been available since 1995. All diesel-powered 100% biodiesel. Biodiesel has some benefits compared to petrodiesel, hydrocarbon fuel derived from crude oil. These benefits include wear and therefore engine lifespan. Biodiesel is a mixture of organic compounds called esters. produced by a chemical reaction between vegetable oils or alcohol At (most commonly present, far more petrodiesel methanol (CH

than 3

OH)). biodiesel is internationally (Figure 16.4.1). Petrodiesel is a non-renewable once used it is not replenished and amounts worldwide animal vehicles Diesel These improved fats can containing which esters and run engine r is are on

an a

o

o biodiesel petrodiesel (7%)

(93%) f

s

FIGURE 16.4.1 total of subject TRANSESTERIFICATION The this structure diesel H

total. of extensive consumption H This of a gap H

typical scientific is likely is biodiesel over research.

to 23 close 000 molecule in ML/year. the is future e

shown Biodiesel as consumed, the are comprises biodiesel depleted. P

resource, both industry only locally Australia’s meaning

400 is ML and

the

in Figure 16.4.2.

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

H

H

H P

H

H

H H g H

H

H

H

H H

H

H

H H

H

O

**H C C FIGURE 16.4.2**

C a C

C

C

C

C C

C

C

C C

C

C

C

H

H

H H

H

H

H H

H

H

O C H

H 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.

447 CHAPTER 16 | FROM FATS AND OILS TO SOAPS AND BIODIESEL

**448**

H

H

C H

AREA OF STUDY 6 | ORGANIC SYNTHESIS: HOW DO CHEMISTS BUILD MOLECULES?

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.

H O

H

H

C O C O

(CH

2

)

14

CH

3

H

(CH

2

H

C O C H

H C H C H C H r

o OH OH OH o + fatty 3CH acid 3 (biodiesel) (CH f methyl 2 )

14

COOCH

esters s 3

g H

C CO O

H

C

e H C H ) 14

CH

3

+ 3CH

3

OH

(CH

2

)

14

CH

3

triglyceride

methanol glycerol (palm oil)

**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

H

H H

H

of with ester triglyceride Triglycerides which triglycerides in this Figure Like relatively is type have an petrodiesel, 16.4.4.

ester are varies only produced produced long sometimes made carbon–carbon depending hydrocarbon H from biodiesel by by P referred plants H a animals, fatty on is single the often H chains acid to not particular such as and form bonds fatty H

a are pure as simple referred unsaturated acid tallow, H in plant substance. the esters, alcohol.

H usually hydrocarbon or to animal as esters because H

fatty The form used like acids. structure saturated chain. carboxylic the O

as A the one fatty However, source. of shown esters, acids acid

the

C C C C C

H

C C C C C C

C C C

H

H

H

H

H

C

H

H

H

H

H

H H O C H P

a

H

H

**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.

methanol catalyst

oil reactor

FIGURE functional methyl two the to The Figure remove One The oil products biodiesel 16.4.5 and 16.4.7. ester of biodiesel groups the water any A makes do flow products, and unreacted not shown chart and and the dissolve glycerol is of glycerol molecule in quite the glycerol, Figure first methanol, in polar. can step each extracted is non-polar. 16.4.6.

in a Conversely, then other the relatively which production be and from This collected is separate small the recycled the of means biodiesel

long molecule separator into separately hydrocarbon that back mixture two in separator with P distinct are the into goes three then separator, as chain the to layers, shown hydroxyl distilled reactor. r on like the the

in

o

A mixture of paraffin oil (coloured

biodiesel

mixture from reactor

FIGURE of production fall economic biodiesel The in the 16.4.7

glycerol P price viability has The of separation resulted produced glycerol. of a

glycerol the g

mostly mostly e biodiesel

glycerol

distillation column

of products of the transesterification process during the manufacture

from this process is about 80% pure. Increased biodiesel in an oversupply of glycerol to the market, leading to a Finding uses for the excess glycerol would increase the biodiesel industry.

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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.

distillation column

biodiesel layer

glycerol layer

separator

449 CHAPTER 16 | FROM FATS AND OILS TO SOAPS AND BIODIESEL

**FIGURE 16.4.6**

unreacted methanol is pumped back to the reactor

**450**

AREA OF STUDY 6 | ORGANIC SYNTHESIS: HOW DO CHEMISTS BUILD MOLECULES?

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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 FIGURE made up e 16.4.8 of many or The potassium spiralled structure (alpha of hydroxide. P

a lipase helix) structures. enzyme r molecule. o The lipase molecule o is a large f protein

s

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.

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451 CHAPTER 16 | FROM FATS AND OILS TO SOAPS AND BIODIESEL

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**452**

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 triglycerides 2

) emissions. that Whether it is produced biodiesel from. produces For example, SO

2

depends soyabean upon oil the origins of the 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.

AREA OF STUDY 6 | ORGANIC SYNTHESIS: HOW DO CHEMISTS BUILD MOLECULES?

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**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 carried Research catalyse principles.

industrial out a continues synthesis using manufacture a base-catalysed to that improve employs of biodiesel the green reaction

use of is chemistry normally lipase s to

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 4 o**

o

f

5 Why not petrodiesel? What lipase-catalysed catalysed Write considered are are an r

the equation the manufacture CO advantages as 2

reaction emissions showing problematic of compared and biodiesel?

the from disadvantages as reaction the those to use the of produced of the base-

biodiesel

of following the

from

triglyceride to produce biodiesel.

H

2

O CO H

H

H

H

g H

H

H

C

e

P

H

H

H

H

H

H

H

H H H

H

H H H

H

H

H

H

H

H

H

H

C

HC

O CO a H

H C

C

C C

C C C C C C C C C C C C C H

H

H

H

H

H

H

H

H

H

H

H

H

H

H H H

H

H H H

H

H

H P

C

H

H

H

H

H

C

C

C C C C C C C C C C C C C C H

H

O

H

2

CO H

H

H

H

H

H

H

H

H

H

H

H

H

H

H H H

H

H H H

HHH

H

H

H

H

H

H

H

C

C

C

C C C C C C C C C C C C C C H

H

453 CHAPTER 16 | FROM FATS AND OILS TO SOAPS AND BIODIESEL

**Chapter review**

KEY TERMS

anionic detergent base hydrolysis biodiesel carboxylate catalyst detergent enzyme ester functional group ester link fatty acid

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

**Production 4 Which A B CH**

CH

3

3

(CH one of 2

**of ) r soaps**

16

the COOH

following o

is the o

formula of a soap?

s

f

monounsaturated fatty acid ester

fatty acid fossil fuel

non-polar green chemistry

non-renewable hard water

petrodiesel hydrolysis

polar hydrophilic

polyunsaturated fatty acid hydrophobic

saponification ion–dipole force

saturated lipid

saturated fatty acid micelle

soap

COOLi P C D (CH 2

)

7

CHCH(CH

2

)

7

COOH).

CH

3

COONa

b Draw the structure of the glyceryl trioleate, showing

CH

3

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

CH

2

CH

CH

2

(CH

2

)

7

CH=CH(CH

2

)

7

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.

H

2

(CH

2

)

16

O

O C O

(CH

2

)

14

CH

3

O

C

(CH

2

)

14

CH

3 O

O C

(CH

2

a Circle an ester functional b Is this triglyceride saturated your answer.

)

14

CH

3 P

a

group. g or unsaturated? e

O

Explain

C O

C (CH

2

)

16

CH

3 O

H

H

C OH

HC

O C (CH

2

)

16

CH

3

+ NaOH H C OH + O

H C OH H

2

C O C (CH

2

)

16

CH

3

H

**454**

AREA OF STUDY 6 | ORGANIC SYNTHESIS: HOW DO CHEMISTS BUILD MOLECULES?

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

CH

2

CH CH

2

OH OH OH b CH

3

(CH

2

)

16

COO CH

2

CH

3

(CH

2

)

16

CH

3

COO CH

(CH

2

)

16

COO CH

2 c CH

3

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

d CH

3

(CH

2

)

*n*

SO

3

–Na+

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 r

o CH

2

following triglyceride.

O

H

2

C O

C (CH

2

)

16

CH

3

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.

reaction for the

P

O

HC

O C (CH

2

)

H

2 C O catalyst

oil P O C chemical a (CH

A 2

)

9

9

CHCH(CH

CHCH(CH g 2

2

)

)

7

CH

3 e +

7

CH

3

separator distillation

chemical A

a Name chemical A. b Name chemical B.

chemical B reactor

biodiesel

455 CHAPTER 16 | FROM FATS AND OILS TO SOAPS AND BIODIESEL

CH

2

CH

2

CH

2

s o CH

2

CH f 2

C O

OH

CHAPTER REVIEW CONTINUED

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.

O

HO C

CH

2

CH

3

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.

H

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

2

CH

3 H O O

C

O C (CH

2

)

14

CH

3

e

O

C

P

r

o (CH

2

)

9

CHCH(CH

o 2

)

7

HC

H

2

C

O

O P palm C C O O

oil a (CH

(CH

2

2

)

)

14

14

CH

CH

3

3 g

**456**

AREA OF STUDY 6 | ORGANIC SYNTHESIS: HOW DO CHEMISTS BUILD MOLECULES?

f

s