

# Chapter 3

# ETHANOL AND BIOFUELS



**Figure 3.1**

Driving after drinking alcohol is dangerous. Breathalyser units use photoconductive cells to measure the concentration of ethanol by determining the amount of light reflected from condensing particles of ethanol. Changes in light intensity affect the conductivity of a photovoltaic cell. The degree to which current intensity drops is used to measure the ethanol concentration in the exhaled breath.

## Introduction

Alkanols are a family of chemicals derived from alkanes. They contain the alcohol functional group ( $\text{—OH}$ ). Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) is an important member of the alkanol homologous series. It is commonly known as ‘alcohol’ or ‘drinking alcohol’. Ethanol is present in beers, wines and spirits. Ethanol is the only simple alcohol that is not toxic. Humans can tolerate small quantities of ethanol; however, it is an addictive drug that depresses the central nervous system. Ethanol is also an important solvent, fuel and component of many medications.

## In this chapter

- |     |          |         |
|-----|----------|---------|
| 3.1 | Ethanol  | page 44 |
| 3.2 | Biofuels | page 50 |

## 3.1 ETHANOL

### Remember

Before beginning this section, you should be able to:

- construct word and balanced formulae equations of chemical reactions as they are encountered
- use models to explain phenomena and/or make predictions.

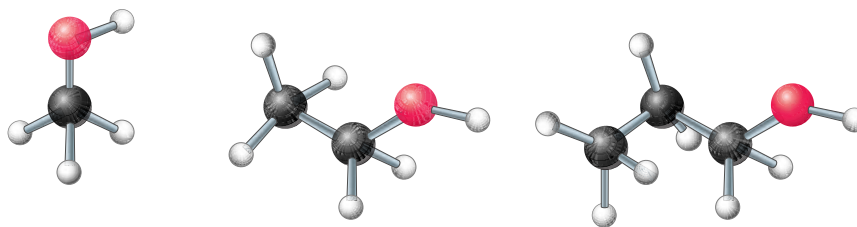
### Key content

By the end of this section, you should be able to:

- identify the IUPAC nomenclature for straight-chained alkanols from C1 to C8
- describe the dehydration of ethanol to ethylene and identify the need for a catalyst in this process, and the catalyst used
- describe the addition of water to ethylene resulting in the production of ethanol, and identify the need for a catalyst in this process and the catalyst used
- describe and account for the many uses of ethanol as a solvent for polar and non-polar substances
- describe conditions under which fermentation of sugars is promoted
- summarise the chemistry of the fermentation process
- process information from secondary sources such as molecular model kits, digital technologies or computer simulations to model (a) the addition of water to ethylene and (b) the dehydration of ethanol
- process information from secondary sources to summarise the processes involved in the industrial production of ethanol from sugar cane
- solve problems, plan and perform a first-hand investigation to carry out the fermentation of glucose and monitor mass changes
- present information from secondary sources by writing a balanced equation for the fermentation of glucose to ethanol.

### The alkanol homologous series

Alkanols are a family or homologous series of compounds that are a sub-set of a larger group known collectively as *alcohols*. All members of the group contain the alcohol functional groups ( $\text{—OH}$ ). Their general formula is:



**Figure 3.2** The first three members of the alkanol homologous series are shown as ball-and-stick models. These models show the bond angles within each molecule. These models are (left to right) methanol, ethanol and propan-1-ol.

The first member of this homologous series is called *methanol*. Figure 3.3 shows the structure of methanol.



**Figure 3.3** The space-filling model of methanol is a more realistic view of methanol's true structure.

### IUPAC nomenclature rules for straight-chain alkanols

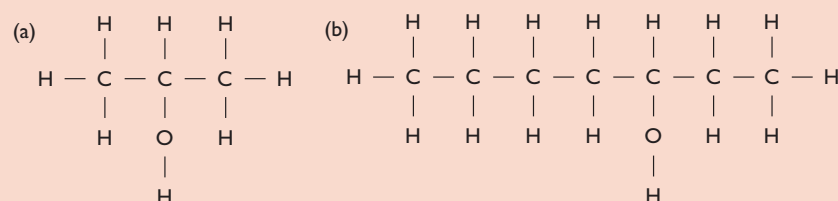
The straight-chain alkanols are named after the corresponding parent alkane. The position of the alcohol functional group is designated by the number of the carbon atom to which it is attached. Because the alcohol group can be located in a number of different positions when the carbon chain has three or more carbon atoms, alkanols can exist in isomeric forms.

#### To name the alkanol:

1. Identify the number of carbons present in the straight chain. Select the correct stem to name the parent alkane. Remove the 'e' and replace it with the suffix 'ol'.
2. For chains with three or more carbon atoms, number the chain from the end so as to give the alcohol group the lowest locant possible.
3. Insert the locant of the  $\text{—OH}$  group in front of the 'ol' suffix. (Note: IUPAC also recognises alternative systematic nomenclature for alkanols in which the locant is inserted in front of the name of the alkanol.)

### SAMPLE PROBLEM 3.1

Name the two alkanols illustrated in Figure 3.4



**Figure 3.4** Use the IUPAC rules to name these alkanols.

### SOLUTION

- (a) The first alkanol has a three-carbon chain and so is derived from propane. It will be called a propanol. The alcohol functional group is on the middle carbon atom (locant = 2 from either end). Thus this alkanol is called propan-2-ol (or 2-propanol).
- (b) The second alkanol has a seven-carbon chain and so it is derived from heptane. It will be called a heptanol. The OH functional group is on the fifth carbon from the left and the third carbon from the right, so its lowest locant is 3. The name of the alkanol is heptan-3-ol (or 3-heptanol).

All members of the alkanol family are toxic to varying extents. Methanol is much more toxic than ethanol. It is added to industrial ethanol to make methylated spirits. The methanol makes the liquid unpalatable.

Table 3.1 lists the molecular formulae and condensed structural formulae of the first five straight-chain alkanols with the OH group on the first carbon atom in the chain.

**Table 3.1** Straight-chain alkanols

$n$	Molecular formula	Condensed structural formula	IUPAC preferred name	Other systematic name
1	$\text{CH}_4\text{O}$	$\text{CH}_3\text{OH}$	methanol	methanol
2	$\text{C}_2\text{H}_6\text{O}$	$\text{CH}_3\text{CH}_2\text{OH}$	ethanol	ethanol
3	$\text{C}_3\text{H}_8\text{O}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	propan-1-ol	1-propanol
4	$\text{C}_4\text{H}_{10}\text{O}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	butan-1-ol	1-butanol
5	$\text{C}_5\text{H}_{12}\text{O}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	pentan-1-ol	1-pentanol

## Ethylene and ethanol

Ethylene can be converted into ethanol via an addition reaction with water. Ethanol can be converted back to ethylene by a catalytic dehydration reaction.

### Converting ethylene to ethanol

Ethanol is commercially prepared by two common methods: indirect hydration and catalytic hydration.

#### Indirect hydration

Ethylene is reacted with 98% sulfuric acid in absorption columns held at 55–80°C and 1–3.5 MPa pressure. The reaction mixture is then mixed with water until the sulfuric acid concentration is about 50% and then heated to 70–100°C. The ethanol that forms is distilled off and has a concentration of 70% (v/v).

The reaction of ethylene with concentrated sulfuric acid occurs in two steps.

1. The sulfuric acid adds onto the ethylene to produce ethyl hydrogen sulfate.



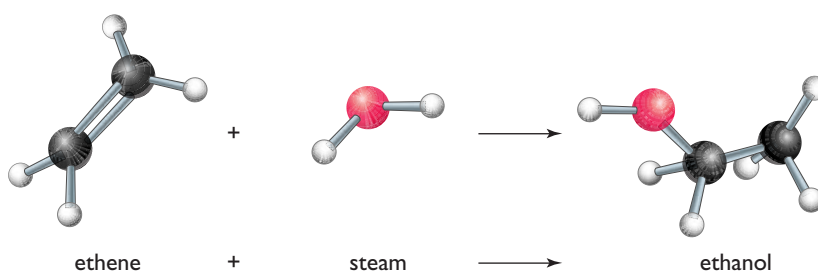
2. The ethyl hydrogen sulfate reacts with water generating ethanol; sulfuric acid is reformed.



### INDIRECT HYDRATION OF ETHYLENE

#### Catalytic hydration

An alternative method of preparing ethanol from ethylene is to pass ethylene and steam over a silica gel or zeolite surface impregnated with phosphoric acid or tungstic acid catalyst. The high pressure (1–9 MPa) used favours the formation of ethanol. The selected temperature (~300°C) is a compromise. At these temperatures the molecules have sufficient kinetic energy to react but the temperature is not too high to reduce the equilibrium yield in this exothermic reaction. The steam concentrations must be kept low to avoid loss of phosphoric acid. Recycling the unreacted vapours over the catalyst and condensing out the ethanol/water as it forms compensates for the low yield of 4% per run. Eventually 97% conversion can be achieved.

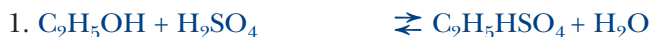


**Figure 3.5**

This structural equation models the formation of ethanol from ethene (ethylene).

#### Converting ethanol to ethylene

Ethanol can be converted back to ethylene by a process called *dehydration*. Concentrated sulfuric acid (or phosphoric acid) is used to remove water from the ethanol molecule. Concentrated sulfuric acid acts as a catalyst and dehydrating agent.



### DEHYDRATION OF ETHANOL

## 3.1 PRACTICAL ACTIVITIES

Modelling  
reactions  
involving  
ethanol



### Properties of ethanol

Table 3.2 summarises the physical properties of ethanol. It is a clear, colourless liquid that has a lower boiling point than that of water. It is also volatile and its vapours form combustible mixtures with air.



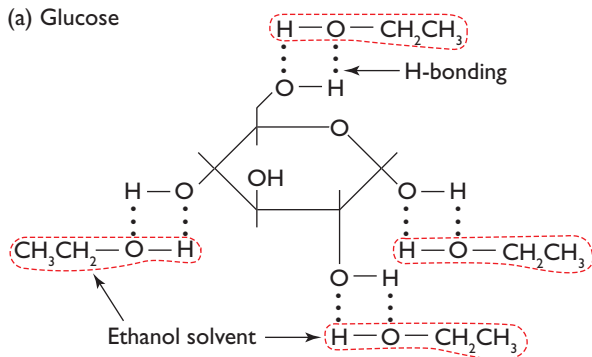
**Table 3.2** Properties of ethanol

Property	Value
melting point	-114.1°C
boiling point	78.3°C
density	0.79 g/mL
solubility in water	miscible in all proportions

Ethanol's major uses are as a motor fuel supplement and as a solvent. Ethanol or ethanol–water mixtures are also used as solvents in cosmetics and toiletries, medications, antiseptics and perfumes. In addition, ethanol is an industrial solvent for lacquers, paints, resins, oils and fatty acids. Its wide use as a solvent is related to the polar nature of the molecule.

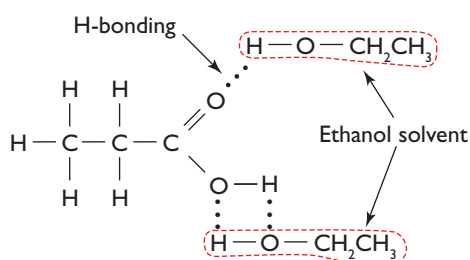
The presence of the alcohol (OH) group determines the characteristic properties of ethanol. Many solutes with polar functional groups (such as other alkanols, esters and carboxylic acids) can strongly interact with the polar ethanol molecule. Some can form hydrogen bonds with ethanol and thus they can dissolve to some extent in this solvent. Ethanol dissolves in water in all proportions due to the strong hydrogen bonding between the two liquids. The non-polar ethyl ( $C_2H_5$ ) group in ethanol assists some low molecular weight non-polar solutes to dissolve in ethanol. This is important in chemistry and pharmacy where alcohol–water mixtures are often used to dissolve various natural oils and organic substances that are normally insoluble in water. Iodine solutions in ethanol–water mixtures have antiseptic properties. The solvent used is a mixture of ethanol and water as non-polar iodine has only a limited solubility in water.

(a) Glucose



The large number of 'OH' groups in glucose causes significant H-bonding with the ethanol solvent.

(b) Propanoic acid



Propanoic acid forms strong hydrogen bonding attachments to the ethanol solvent.

**Figure 3.6**

The H of the OH group in ethanol can hydrogen bond with water or other ethanol molecules.

## Fermentation

**fermentation:** the biochemical reaction in which sugars are converted into ethanol and carbon dioxide under the action of an enzyme (produced by microbes such as yeast or bacteria)

Since ancient times, the process of **fermentation** has been used to prepare ethanol. Simple sugars derived from plant material are mixed with yeast and the *zymase*, *maltase* and *invertase* enzymes produced by the yeast catalyse a complex series of biochemical reactions in which the sugars are ultimately converted to glucose and then to ethanol and carbon dioxide. The reaction is exothermic and heat must be dissipated (via heat exchangers) to ensure that the yeast does not die. Yeast is an aerobic organism but

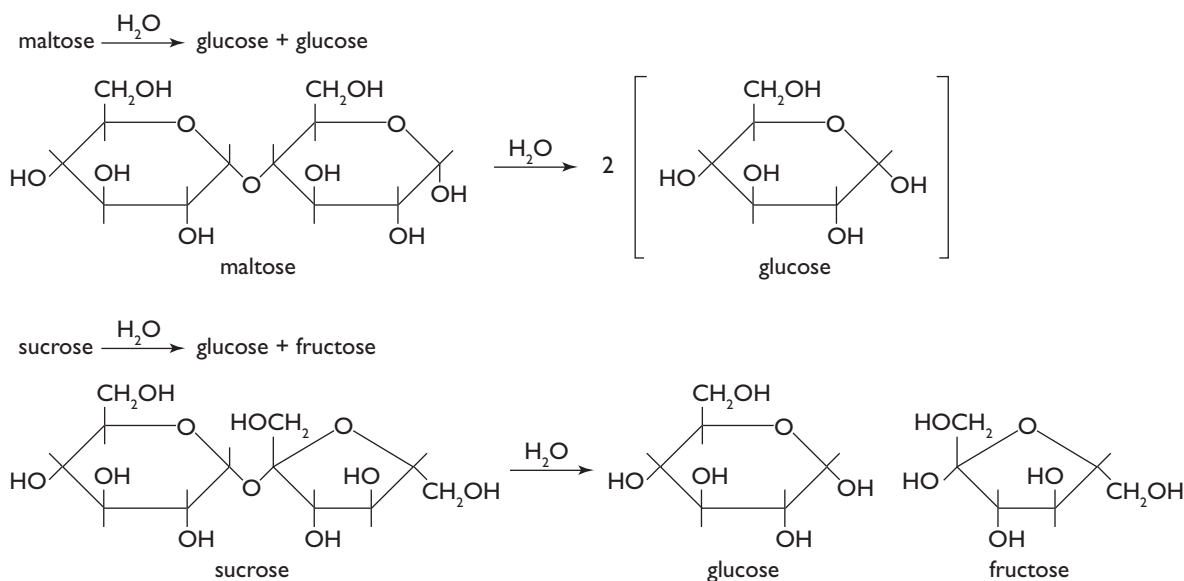
**anaerobic:** a process occurring in the absence of air



**Figure 3.7**  
Alcoholic beverages such as beer have been prepared for thousands of years using the process of fermentation

when deprived of oxygen it will respire the sugars anaerobically to obtain energy. Any oxygen present in the reaction vessel is quickly used up by the growing and reproducing yeast cells and the conditions change to anaerobic. As **anaerobic** fermentation continues, the bubbles of carbon dioxide escape from the fermenting mixture. Fermentation stops when the available sugars are metabolised. A small residue of sugar usually remains.

More-complex carbohydrates (e.g. starch) can also be fermented. The enzyme *diastase* from germinating barley is used to break starch down to maltose. The *maltase* enzymes convert the maltose to glucose. The *zymase* enzymes in the yeast then convert the glucose to ethanol and carbon dioxide. In northern Australia, vast amounts of sugar cane are grown. One important by-product of the sugar industry is molasses syrup that contains a high percentage of sucrose. The molasses is used to produce ethanol by hydrolysis and fermentation. Yeast also produces an enzyme called *invertase* that breaks sucrose down to form glucose.



**Figure 3.8**

Maltose and sucrose are disaccharides that can be broken down to simple monosaccharides.

### Fermentation materials and conditions

The following information summarises the common fermentation materials and the conditions required for fermentation:

- alcohol-tolerant yeast (*Saccharomyces ellipsoideus*)
- aqueous solution of simple sugars (containing 30–50 ppm sulfur dioxide to kill bacteria)
- pH: 3.7–4.6 (low pH prevents pathogens from growing)
- diammonium phosphate (N, P nutrient) to aid growth of yeast
- temperature: ~37°C (more rapid bulk fermentation of sugars derived from molasses or other grain starches)
  - ~22–30°C (red wines)
  - ~25°C (white wines)
  - ~15°C (champagne)

- time: 3–5 days (for ethanol produced from grain starch fermentation)  
10–30 days (white wine)
- anaerobic conditions (closed vessels; absence of air).

Enzymes are protein catalysts. They are highly pH- and temperature-sensitive and will *denature* (break down) in most cases if heated above 40°C. Fermentation is also an anaerobic process. If oxygen or air is present, the yeast uses the sugars and oxidises them to carbon dioxide and water. The presence of bacteria (*Acetobacter*) in the fermentation vats can turn the wine to vinegar overnight, so a sulfite solution (source of sulfur dioxide) is added to kill any bacteria.

Yeast mould occurs naturally. For example, the white, fuzzy appearance on the skins of mature grapes is a wild yeast fungus. Traditional wine making involves the yeast, which is on the grape skin, acting on the sugars present in the grape juice. Different varieties of grapes and strains of yeast produce differently flavoured wines. Not all yeast strains are as tolerant to alcohol as wine-making strains. Winemakers over hundreds of years of research have developed alcohol-tolerant yeast strains that will not die until the alcohol concentration reaches 15% (v/v) during fermentation. Thus, many wines that are marketed in Australia typically have alcohol concentrations between 12% (v/v) and 14% (v/v). Recent research in Sweden has led to the development of yeast strains that are tolerant of high temperatures and high sugar concentrations, and which will produce up to 14% (v/v) alcohol at 40°C and up to 17% (v/v) alcohol at 38°C.

Fortified wines (e.g. sherry, port) are wines that have an alcohol content greater than 14% (v/v). Halfway through the fermentation process for red wine, a distilled alcoholic spirit (~95% ethanol) is added to raise the alcohol content to that required for sherry or port 18–24% (v/v). This causes fermentation to cease as the yeast cells die. Distillation is used to produce spirits with alcohol contents ~35–40% (v/v) higher than those of fortified wines. Fractional distillation methods are used to reach very high concentrations ~96% (v/v) of ethanol. Due to the strong hydrogen bonding between ethanol and water, water cannot be completely removed by these methods.

### 3.2 PRACTICAL ACTIVITIES

Fermentation



### 3.4 DATA ANALYSIS

Industrial preparation of ethanol from sugar cane



The sale of alcohol was made illegal in the USA between 1919 and 1933. This period was called the *Prohibition era*.

## SYLLABUS FOCUS

### 8. USING INSTRUCTION TERMS CORRECTLY

When answering questions it is important to know what the instruction terms ('verbs') require you to do. Here is an example:

#### 'Justify'

This verb requires you to support an argument or conclusion.

#### Example:

Justify the need to use dehydrating agents rather than further fractional distillation to produce absolute alcohol from fermented sugar solutions.

#### Answer:

Repeated fractional distillation of alcoholic solutions produces a mixture that contains only 96% ethanol. This is because of the strong hydrogen bonding that exists between water and ethanol. A mixture called an *azeotrope* is formed. Distillation of the azeotrope produces a vapour of the same composition. To remove the last amount of water, the 96% ethanol must be passed through dehydrating material that will absorb the water.

## 3.1 Questions

1. Write the condensed structural formulae and name for all the straight-chain alkanols in which the functional group is on the terminal carbon atom, and that contain:  
(a) six carbon atoms (b) eight carbon atoms.
2. Heptan-1-ol has a number of straight chain isomers. Name these isomers.
3. Describe the industrial method for the conversion of:  
(a) ethylene to ethanol  
(b) ethanol to ethylene.  
For each reaction write the overall equation for the process.
4. Explain why the hydration of ethylene is not carried out at high temperatures.
5. Ethanol is less dense than water. Explain why ethanol does not float on water.
6. The solubility of alkanols decreases with increasing chain length. Explain why the solubility of heptanol and octanol is increased by adding ethanol to the water.
7. (a) Write a balanced equation for the fermentation of glucose.  
(b) Calculate the theoretical percentage by weight of ethanol that is produced by fermentation of glucose.  
(c) In practice, the yield of ethanol is only 47% by weight. Account for this lower yield.
8. The label on a can of beer showed that it contained 5% (v/v) ethanol. Calculate the volume of ethanol that would be present in one dozen 500 mL cans of beer?
9. A mixture of sucrose and maltose is to be fermented. Describe the enzymes that are required to produce ethanol from this mixture.
10. Justify the conditions required for the fermentation of grape juice to produce white wine.

## 3.2 BIOFUELS

### Ethanol as a fuel

#### Remember

Before beginning this section, you should be able to:

- construct word and balanced-formula equations of chemical reactions that you encounter
- discuss the need for alternative sources of the compounds presently obtained from the petrochemical industry.

#### Key content

By the end of this section, you should be able to:

- outline the use of ethanol as a fuel and explain why it can be called a renewable resource
- define the molar heat of combustion of a compound and calculate the value for ethanol from first-hand data
- assess the potential of ethanol as an alternative fuel and discuss the advantages and disadvantages of its use
- process information from secondary sources to summarise and evaluate the use and success of ethanol as an alternative car fuel
- identify and choose data sources and perform a first-hand investigation to determine and compare heats of combustion (per gram and per mole) of at least three liquid alkanols.

During the 1980s, various governments introduced legislation that led to the development of cleaner burning fuels that would reduce the levels of air pollution. The development of renewable biofuels or fuel additives such as ethanol from biomass is an important area of research. Ethanol is a renewable fuel as it can be manufactured from carbohydrates such as glucose and starch that are produced by the process of photosynthesis in green plants.

During photosynthesis, carbon dioxide becomes incorporated into carbon compounds in the plant. When ethanol, derived from biomass, is burnt as a fuel the carbon dioxide is returned to the atmosphere. The process of generating biofuels such as ethanol from biomass is not 'greenhouse neutral'. The energy input required for cultivation, production of fertilisers, distillation of the fermented sugars and disposal of fermented waste products comes from the combustion of fossil fuels or biomass. This leads to the release of carbon dioxide. Compared with the combustion of petrol, however, the combustion of ethanol has a lower greenhouse impact.

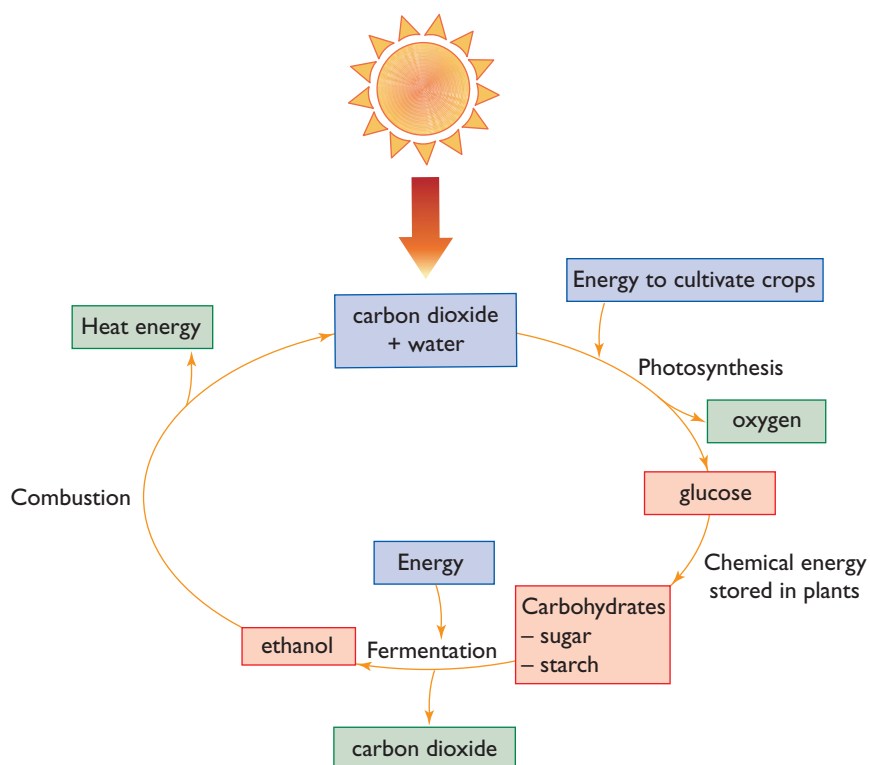
Brazil is the world's largest producer of ethanol. Since 1975 Brazil has implemented a biofuels program. In Brazil, sugar cane has been used as a source of sugar for alcoholic fermentation. The cellulose waste (called *bagasse*) is also used to generate ethanol. Two forms of ethanol are produced: anhydrous ethanol and hydrous ethanol. The anhydrous ethanol is used as a 24% blend with petrol, and no engine modifications are needed. Hydrous alcohol contains some water and engine-modified cars are required to utilise this fuel. Brazil has struggled in its attempts to implement a biofuels program because of political and economic pressures and the higher costs of producing ethanol compared with petrol. Subsidies needed to be introduced to protect sugar growers and engine manufacturers.





**Figure 3.9**

In Australia, some of the molasses produced is used to make ethanol. This ethanol can be used as a solvent or a fuel.



**Figure 3.10**

Carbon dioxide is used by plants to make sugars. Sugars can be fermented to produce ethanol. Ethanol burns and releases carbon dioxide back into the air.

The use of ethanol as a car fuel dates back to the 1880s when Henry Ford in the USA designed a car that ran entirely on ethanol.

Starch and simple sugars derived from wheat and corn are important biomass feedstocks. A biofuels program has been adopted in the USA. This initiative grants tax concessions to ethanol producers. Two processes are commonly used in Canada and the USA to convert corn waste to ethanol: dry milling and wet milling. In the dry milling process, the entire corn mash is fermented. The ground corn feedstock is cooked in water and then enzymes such as *amyloglucosidase* are added. The enzyme promotes the hydrolysis of the starch to form glucose. Following this step, the glucose is fermented using yeast (*Saccharomyces cerevisiae*) and ethanol is produced. Distillation of the reaction mixture yields a product that is 95% ethanol. In order to use the ethanol as a petrol additive, the remaining water must be removed. In the wet milling process the corn is soaked in a mixture of water and sulfur dioxide before the corn oil is extracted from the starch. The starch is then processed as for the dry milling process.

Ongoing research has identified possible methods of production of ethanol from cellulosic feedstocks such as cornfield residues and waste paper. Chemists are investigating efficient methods of hydrolysing cellulose to glucose as well as determining which microbes are most effective in fermenting the 4-carbon and 5-carbon sugars produced from the hydrolysis reactions. Genetically modified *E. coli* strains have been investigated. Improved technology such as membrane filtration systems (that retain enzymes and yeast but allow water, ethanol and glucose to pass through) have helped the development and commercialisation of this process.

### Advantages and disadvantages of ethanol as a fuel

Ethanol has several advantages and disadvantages as a fuel. One advantage related to the greenhouse effect was discussed above. Let us now examine some of the key issues related to ethanol's suitability as a fuel. Table 3.3 provides information on the properties of ethanol related to its use as a fuel.

**Table 3.3** Fuel properties of ethanol

Property	Value
vapour pressure (at 25°C)	10 kPa
flash point	+13°C
ignition temperature	+365°C
flammability limit of vapour in air	3.3–19% (v/v)
enthalpy of vaporisation	43 kJ/mol
enthalpy of combustion	–1367 kJ/mol

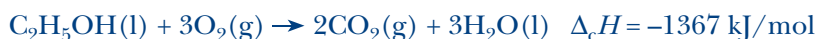
**molar heat of combustion:** the heat energy released when one mole of a substance is burnt in excess oxygen to produce products in their standard states\*.

\*measured under standard conditions of temperature (25°C) and pressure (100 kPa)

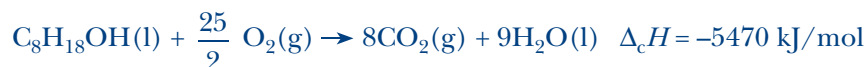
### Heat of combustion

Ethanol is energy-dense but does not release as much energy as petrol on complete combustion. Because it burns more efficiently and completely than petrol in a car engine, the amount of energy available for mechanical work from a 10% ethanol blend is almost the same. The following equations compare the molar enthalpies of combustion of ethanol and octane.

Complete combustion of ethanol:



Complete combustion of octane (petrol component):



When ethanol burns in air it burns more completely than octane under the same conditions. The stoichiometric equations above show that for each mole of fuel, octane requires considerably more oxygen for complete combustion but it also produces more energy on a molar basis. Longer-chain alkanols burn less efficiently than the shorter-chain alkanols and produce more soot and carbon monoxide.

### SAMPLE PROBLEM 3.2

### SOLUTION

- (a) Compare the energy released from the combustion of 1 kg of ethanol and 1 kg of octane.  
 (b) The driving ranges of two identical cars, fuelled with equal masses of ethanol and octane, are to be compared. Explain which fuel will lead to the greater driving range.

- (a) Calculate the energy released by each fuel.

For ethanol:

$$M_{\text{ethanol}} = 46.1 \text{ g/mol}; n = m/M = 1000/46.1 \\ = 21.69 \text{ mol}$$

(where  $M$  is the molar weight,  $m$  is the mass and  $n$  is the number of moles).

$$\text{Heat released per kilogram} = n\Delta_c H = (21.69)(1367) = 29650 \text{ kJ} \\ = 29.7 \text{ MJ}$$

For octane:

$$M_{\text{octane}} = 114.2 \text{ g/mol}; n = m/M = 1000/114.2 \\ = 8.76 \text{ mol}$$

$$\text{Heat released per kilogram} = n\Delta_c H = (8.76)(5470) = 47917 \text{ kJ} \\ = 47.9 \text{ MJ}$$

- (b) The combustion of the octane produces more energy per kilogram. Thus more energy is available for the conversion to mechanical energy. The octane fuelled car will be able to travel a greater distance than the ethanol fuelled car.

**flash point:** the minimum temperature at which the vapour pressure of the fuel is just enough to form a combustible mixture in air

**ignition temperature:** the minimum temperature to which a combustible fuel–oxidiser mixture must be heated for it to ignite spontaneously

### 3.5 DATA ANALYSIS

Ethanol as an alternative fuel

#### Combustible mixtures

The **flash point** of ethanol is higher than that of petrol ( $-43^\circ\text{C}$ ). Therefore, combustible mixtures of ethanol vapour are not as readily formed in cold climates. Ethanol's **ignition temperature** is lower than that of petrol ( $390\text{--}420^\circ\text{C}$ ), so a combustible mixture will more readily ignite. Ethanol has a wider flammability limit in air compared with that of petrol ( $1.4\text{--}7.6\%$ ). Thus a 10% mixture of petrol vapour and air is too high a fuel concentration to ignite, whereas a 10% mixture of ethanol vapour and air will ignite and burn.

#### Combustion efficiency

Mixtures of ethanol and petrol do boost the octane rating of the fuel. This rating measures the degree to which the fuel burns efficiently and reduces engine knock from premature and uncontrolled combustion. Ethanol is an excellent solvent for many compounds. Therefore, deposits that have built up over time with petrol use may dissolve after using ethanol-blended petrol. Fuel filters may need to be changed after 500 km when ethanol is being used. Continued use of ethanol produces a cleaner system.

#### Ethanol as a petrol extender

From 10–20% of anhydrous ethanol is added to petrol (without engine modifications) to produce a fuel mix called 'gasohol'. This fuel mixture is sold in many countries as a petrol extender. A benefit of gasohol is that it reduces the use of non-renewable oil.

### 3.3 PRACTICAL ACTIVITIES

Heats of combustion of alkanols



#### Engine modifications

When hydrous alcohol or higher concentrations of anhydrous alcohol in petrol are used, a higher engine compression ratio is required in order to utilise ethanol's higher octane rating. Engine modifications are expensive. High compression ratios lead to greater wear on the engine and a shorter engine life. Ethanol does burn more cleanly and less carbon is deposited in the engine. Consequently, spark plugs last longer.

#### Arable land

In some parts of Australia (such as Queensland) the ethanol–petrol blend is marketed as 'petranol'. Australia lacks the arable land to grow sufficient sugar cane crops to make ethanol an important contributor to our liquid fuel demands. On a worldwide basis, double the area of arable land would be needed to produce sufficient ethanol to meet demand.

The use of biofuels such as ethanol enjoy political support around the world. In many cases, however, this support is not translated into action.

#### SAMPLE PROBLEM 3.3

A group of students used an aluminium calorimeter in their experiment to determine the molar heat of combustion of pentan-1-ol. The following set of data was collected.

Volume ( $V$ ) of water in calorimeter = 200 mL

Density ( $D$ ) of water = 1.0 g/mL

Mass ( $m$ ) of aluminium calorimeter = 30.0 g

Initial temperature of water = 22.5°C

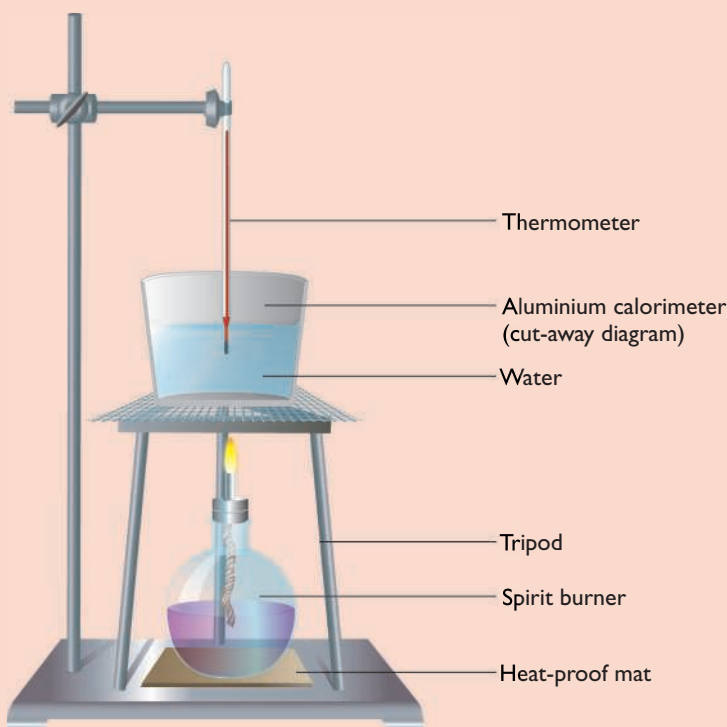
Final temperature of water = 29.5°C

Initial mass of spirit burner = 222.50 g

Final mass of spirit burner = 222.31 g

Specific heat capacity of water = 4.18 J/(g.K)

Specific heat capacity of aluminium = 0.90 J/(g.K)



**Figure 3.11** The heat from the combustion of the alkanol is absorbed by water in a calorimeter.



**SOLUTION**

- (a) Assuming that the calorimeter and the water have the same initial and final temperatures, calculate the molar heat of combustion of pentan-1-ol.
- (b) Explain why the experimental value for the molar heat of combustion deviates significantly from the literature value (3331 kJ/mol).

- (a) Calculate the heat released from the fuel by calculating the heat absorbed by the calorimeter and its contents.

Step 1. Calculate the mass of water

$$\begin{aligned}\text{Mass} &= DV = (1.00)(200) \\ &= 200 \text{ g}\end{aligned}$$

Step 2. Calculate the total enthalpy change

$$\begin{aligned}\Delta H &= [-Cm\Delta T]_{\text{water}} + [-Cm\Delta T]_{\text{aluminium}} \\ &= [-(4.18)(200)(29.5 - 22.5)] + [-(0.90)(30.0)(29.5 - 22.5)] \\ &= [-5852] + [-189] \\ &= -6041 \text{ J}\end{aligned}$$

Step 3. Calculate the heat of combustion per gram of fuel.

$$\text{Mass of fuel burnt} = 222.50 - 222.31 = 0.19 \text{ g}$$

$$\begin{aligned}\Delta H &= -6041 \text{ J} / 0.19 \text{ g} \\ &= -31795 \text{ J/g} \\ &= -31.8 \text{ kJ/g}\end{aligned}$$

$$\text{Heat of combustion (per gram)} = 31.8 \text{ kJ/g.}$$

Step 4. Calculate the heat of combustion per mole of fuel.

$$M_{\text{pentan-1-ol}} = 88.3 \text{ g/mol}$$

$$\begin{aligned}\text{Moles of pentan-1-ol} = n &= m/M = 0.19/88.3 \\ &= 2.152 \times 10^{-3} \text{ mol}\end{aligned}$$

$$\begin{aligned}\Delta H &= -6041 / 2.152 \times 10^{-3} = -2.8 \times 10^6 \text{ J/mol} \\ &= -2800 \text{ kJ/mol}\end{aligned}$$

$$\text{Molar heat of combustion} = 2800 \text{ kJ/mol}$$

- (b) The combustion reaction was incomplete. Some CO and soot were produced, which means that less than the maximum energy is released per mole. Also, significant heat is lost to the surrounding air.

## SYLLABUS FOCUS

### 9. USING INSTRUCTION TERMS CORRECTLY

When answering questions it is important to know what the instruction terms ('verbs') require you to do. Here is an example:

#### 'Predict'

This verb requires you to suggest a result or outcome based on available evidence.

#### Example:

A student measures the molar heat of combustion of propan-1-ol, butan-1-ol, methanol and hexan-1-ol using spirit burners and calorimeters. Predict which alkanol will generate the greatest molar heat on combustion in a spirit burner.

#### Answer:

The prediction is hexan-1-ol. This has the largest molecule with the highest molar weight and the greatest number of C—C and C—H bonds. This molecule has the greatest chemical potential energy stored in its bonds and therefore more energy to release per mole on combustion.

## 3.2 Questions

1. Generating a biofuel such as ethanol from biomass is not 'greenhouse neutral'. Explain.
2. (a) Identify biomass feedstocks that can be used to produce ethanol.  
(b) Explain how biomass can be converted to ethanol.
3. (a) A sample of ethanol vapour in air has a concentration of 20% (v/v). Explain whether such a mixture will combust in the presence of an ignition source at room temperature.  
(b) Write a balanced equation for the complete combustion of ethanol in air.  
(c) The molar enthalpy of combustion is  $-1367 \text{ kJ/mol}$ . Calculate the heat energy released on the complete combustion of 100 litres of pure ethanol. (The density of ethanol is  $0.785 \text{ g/mL}$ .)
4. Explain why ethanol is not as suitable a fuel as petrol in icy conditions.

5. Explain how ethanol can be used as a 'petrol extender'.
6. Calculate the heat released when 5.0 g of butan-1-ol burns completely in oxygen. (The molar enthalpy of combustion of butan-1-ol is  $-2676 \text{ kJ/mol}$ ).
7. The flammability limits in air of ethanol, methanol and two other liquid hydrocarbon fractions (A and B) are compared.

Fuel	Flammability limits (% v/v)	Heat vaporisation (kJ/mol)
ethanol	3.3–19	43
methanol	6.0–36.0	38
A	1.5–5.5	62
B	1.1–7.5	52

Predict which fuel vapour is more likely to produce combustible mixtures with air over a range of environmental conditions.



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CHECKPOINT  
REVISION I

## SUMMARY

- Alkanols are a family or homologous series of compounds that are a sub-set of a larger group known collectively as alcohols.
- IUPAC nomenclature is used to name alkanols. They are named after their parent alkane. The '-ol' suffix and the locant (if required) are placed after the stem and before the suffix '-ol', such as butan-2-ol.
- Ethylene can be converted to ethanol by two methods. One method involves indirect hydration using sulfuric acid in absorption columns. A second method uses catalytic hydration in which ethylene and steam pass over a solid catalyst impregnated with phosphoric acid.
- Ethanol can be converted back to ethylene by dehydration using concentrated sulfuric acid or phosphoric acid.
- Ethanol is a clear, colourless liquid whose boiling point is lower than that of water. It is a useful solvent and fuel.
- Ethanol can be manufactured by the fermentation of sugars using yeast. This process involves anaerobic respiration.
- Ethanol is a useful solvent in medicines and in industry because it is a polar molecule.
- Ethanol is used as a fuel extender and as a biofuel in some countries. Ethanol does not release as much energy per mole as petrol, but it burns more cleanly.

# PRACTICAL ACTIVITIES

## 3.1

### PRACTICAL ACTIVITIES



## MODELLING REACTIONS INVOLVING ETHANOL

### Aim

To model the addition of water to ethylene and the dehydration of ethanol

### Materials

- ball-and-stick molecular model kits

### Method

#### Part A: Hydration of ethylene

- Use the molecular model kit to make models of the following molecules:

- $C_2H_4$
- $H_2O$
- Acid catalyst ( $H-X$ ). (Use a coloured ball to represent group  $X$ , which is the rest of the acid molecule;  $X = HSO_4$  in sulfuric acid or  $X = H_2PO_4$  in phosphoric acid.)

- Select the ethylene and acid catalyst molecules. Break one of the bonds joining the carbon atoms and break the  $H-X$  bond.
- Join the  $H$  atom onto first carbon and the  $X$  group onto the second carbon.
- Select your water molecule and break it to produce a hydrogen atom and an  $-OH$  group.
- Remove the  $X$  group from the model (step 3) and reform the  $H-X$  acid catalyst molecule.
- Join the  $-OH$  group onto the second carbon to form the ethanol molecule.

#### Part B: Dehydration of ethanol

- Use your models of ethanol and  $HX$  from Part A.

- Remove the  $-OH$  group from the ethanol molecule and break the  $H-X$  bond. Attach the  $H$  atom to the  $OH$  group to form a water molecule.
- Attach the  $X$  group to the carbon atom to form  $CH_3CH_2X$ .
- Remove the  $X$  group and an  $H$  atom from the molecule and create a double bond between the carbon atoms to form the ethylene molecule. Join the  $H$  and  $X$  atoms to reform the acid catalyst,  $HX$ .

### Questions

Answer the following questions in your report on this experiment.

- Write balanced stepwise equations for the two reactions that were modelled.
- Figure 3.12 shows steps in the hydration of ethylene (based on the method above) but they are shown in random order. List the steps in their correct order.

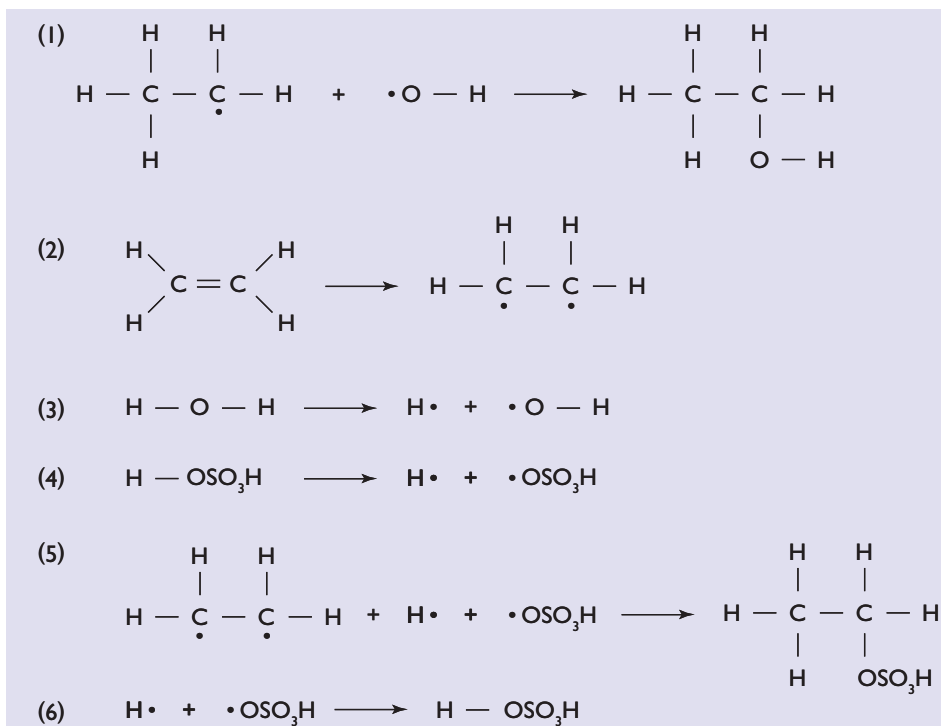


Figure 3.12 Use this information to answer question 2.

- Draw structural formulae based on your models of ethylene and ethanol.

# PRACTICAL ACTIVITIES

## 3.2

### PRACTICAL ACTIVITIES



## FERMENTATION

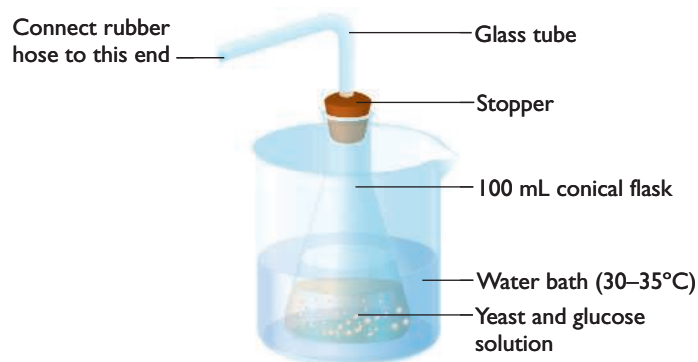
### Aim

To ferment a glucose solution and to monitor the mass changes involved

### Materials

For each group:

- 100 mL conical flask with rubber stopper and bent glass tube (see diagram)
- 500 mL beaker
- 50 mL measuring cylinder
- large test tube
- 20 mL glucose solution 10% (w/v)
- 1.0 g dried yeast (baker's or brewer's yeast)
- limewater
- thermometer
- electronic balance
- equipment needed for the control



**Figure 3.13** Glucose solution can be fermented in this apparatus using yeast.

### Safety

- Wear safety glasses throughout this experiment.
- Identify the other safety precautions that are relevant to this experiment by reading the method.

### Method

Read the method below and decide in your work groups the control that needs to be included in the

experimental design. Prepare the control and use it as part of your experiment.

1. Weigh out 1.0 g of yeast onto a square of paper and add it to the 100 mL conical flask.
2. Measure 20 mL of glucose solution using a measuring cylinder and add the glucose solution to the flask.
3. Insert the stopper and the bent glass tube. Dry the outside of the flask with a paper towel.
4. Weigh the apparatus on an electronic balance and record the initial mass.
5. Place the reaction apparatus in a 500 mL beaker containing some water that is held at 30–35°C throughout the lesson. The warm water will accelerate the fermentation process.
6. After 30 minutes, remove the flask and dry it carefully before weighing it. Observe the appearance of the fermenting mixture. Return the flask to the warm water.
7. During the next half of the lesson connect a rubber hose to the bent glass tube and allow any gas to pass into a tube containing some limewater. Observe the change in appearance of the limewater. Remove the hose.
8. Repeat step 6 near the end of the lesson and record the new mass.
9. Leave the flask until the next lesson (preferably in a warm place at 30–35°C). During the next lesson reweigh the flask and record the final mass. Remember to treat the control in the same way.

### Questions

Answer the following questions in your report on this experiment.

1. Calculate the total change in mass and account for these changes.
2. Justify the choice of control used in this investigation.
3. Limewater is a solution of calcium hydroxide. Write a balanced equation for the reaction that occurred with the limewater.
4. Discuss the validity of the method used.
5. Write the balanced equation for the fermentation of glucose.
6. Use your experimental results to calculate the mass of ethanol that must have formed by the fermentation of the 20 mL of 10% (w/v) glucose solution. State the assumptions you are making in the calculation.



# PRACTICAL ACTIVITIES

## 3.3

### PRACTICAL ACTIVITIES



## HEATS OF COMBUSTION OF ALKANOLS

### Aim

To perform first-hand investigations in the school laboratory to determine the heats of combustion of selected alkanols and to use this information and gathered literature data to determine the heat of combustion for a longer-chain alkanol.

### Background

The calorimetry equation ( $\Delta H = -Cm\Delta T$ ) can be used to calculate the heat of combustion of a fuel. If a known mass of fuel is burnt and the heat evolved is used to heat a container of water of known mass, then the rise in temperature of the heated water and vessel can be used to estimate the heat of combustion of the fuel. The heat evolved from the burning fuel not only heats the water ( $\Delta H_{\text{water}}$ ) but the vessel containing the water ( $\Delta H_{\text{vessel}}$ ) and the air surrounding the apparatus. The heat lost to the air cannot easily be measured and is part of the error in estimating  $\Delta H$  in this experiment. Draught excluders may help to reduce the heat loss.

In this experiment we make the assumption:

$$\Delta H = \Delta H_{\text{water}} + \Delta H_{\text{vessel}} = (-Cm\Delta T)_{\text{water}} + (-Cm\Delta T)_{\text{vessel}}$$

In your experimental design you will need to gather second-hand data for the specific heat capacity of water and the material of your vessel. Chemical data books may be provided by your teacher, or you can locate this information by an Internet search. Your teacher may also provide you with MSDS forms to do a risk analysis, or you may be required to gather this information yourself.

### Method

#### 1. Materials

Your group is provided with three spirit burners containing methanol, ethanol and propan-1-ol (1-propanol). You are also provided with a tray

of the following materials that can be used to construct an apparatus to heat 150 mL of water in a suitable container using the heat liberated from the combustion of alkanols in the spirit burners. Some equipment will *not* be used.

100°C thermometer	50°C thermometer
glass stirring rod	tripod
250 mL pyrex conical flask	copper beaker
aluminium beaker (can)	boss-heads
clamps	stands
electronic balance	Bunsen burner
gauze	ruler
heat-proof mats	large cardboard sheets

#### 2. Group decisions

In your groups:

- design the apparatus that you will use to measure the heat of combustion of each alkanol
- decide how your method will minimise heat loss and control variables
- identify how reliability and accuracy can be improved
- use the material safety data sheets (MSDS) provided by your teacher to identify risks and to complete a risk assessment.

#### 3. Class discussion

Each group should report back to the class and describe the final apparatus and procedures adopted. Further adjustments to the plan may be needed.

Write up a final method for the experiment.

#### 4. Performing the experiment

- Set up your apparatus according to the method. Draw up a table and record the mass of the vessel, water and spirit burner (initial mass).
- Select the first alkanol burner and light the wick. Record the rise in temperature (say 10°C) of the stirred water and extinguish the flame safely. Reweigh the spirit burner.
- Repeat the experiment with the first alkanol a sufficient number of times (according to your agreed method).
- Repeat the procedure for the other alkanols.

# PRACTICAL ACTIVITIES

## Results and analysis

1. For each alkanol, use the calorimetry equation to calculate the heat (in joules) absorbed by the water and the vessel. Assume the rise in temperature of the water is equal to the rise in temperature of the vessel.
2. For each alkanol, calculate the mass of each fuel burnt.
3. Calculate the heat of combustion per gram of each alkanol.
4. Calculate the heat of combustion per mole of each alkanol.
5. Compare your results with the accepted literature values listed below:  
Molar heats of combustion:  
    methanol: 726 kJ/mol  
    ethanol: 1367 kJ/mol  
    propan-1-ol: 2021 kJ/mol
6. Plot a line graph of your experimental molar heat of combustion data versus molar weight of each alkanol. Draw the line of best fit through the data and extrapolate the line to obtain a value for the molar heat of combustion of butan-1-ol (or, 1-butanol).

7. On the same grid plot the literature values for the molar heats of combustion of the alkanols versus molar weight. Include the molar heat of combustion of butan-1-ol (2676 kJ/mol). Draw a line through the data points. By what percentage did your extrapolated data deviate from the accepted value for butan-1-ol?
8. Use your graphs to estimate the accuracy in your determination of the molar heats of combustion by determining the average percentage error. Account for the errors in the measurements.
9. Identify the major risks in this investigation.

## Conclusion

Write an appropriate conclusion for this experiment.

# DATA ANALYSIS

## 3.4 DATA ANALYSIS

### INDUSTRIAL PREPARATION OF ETHANOL FROM SUGAR CANE

Read the following information and then answer the questions that follow.

In northern NSW and Queensland, sugarcane is grown to produce sugar (sucrose). A by-product of the sucrose production is a concentrated solution of sucrose called molasses. Some of this molasses syrup can be used to produce ethanol by fermentation. The steps involved are summarised below.

- Crush the harvested sugarcane to extract the juices that contain sucrose.
- Following the extraction and crystallisation of sucrose the remaining liquor (molasses) contains a high percentage of sucrose.
- Water is added to the molasses syrup to reduce the sucrose concentration to about 40%. Acid is then added to obtain an acidic medium (pH ~4–5) that prevents bacterial growth.
- The mixture in the fermentation tank (*fermenter*) is adjusted to the desired temperature (~32–37°C) and an appropriate alcohol tolerant yeast (e.g. *Saccharomyces cerevisiae*) is added.
- Vigorous fermentation begins and considerable amounts of carbon dioxide are evolved. The gas

is collected and purified and sold to other industries such as the soft-drink industry.

- After about 2 days the fermentation is complete. The mixture now contains about 8–12% ethanol. The mixture is passed through rectifying columns to purify it.
- The final mixture is pumped to the distillery and distilled. Steam produced from the combustion of sugarcane waste (*bagasse*) is used to heat the distillation vessels. The distillate produced is ~96% ethanol.
- Anhydrous ethanol can be obtained by additional dehydration steps.

#### Questions

1. Explain why the pH of the fermenting mixture is adjusted to produce an acidic medium.
2. Explain why the temperature of the fermenter is kept between strict limits.
3. (a) Identify the gas that is produced during fermentation.  
(b) Explain why this gas is not released to the air as a waste product.
4. State one use of the waste sugarcane stems and leaves.
5. Identify the physical process that is used to extract the ethanol from the purified fermented mixture.
6. Explain why baker's yeast would not be suitable for the production of ethanol from molasses.

# DATA ANALYSIS

## 3.5 DATA ANALYSIS

### ETHANOL AS AN ALTERNATIVE FUEL

Read the following information and then answer the questions that follow.

When Henry Ford established the Ford motor company in the early twentieth century he believed that renewable ethanol would be the logical fuel to power his vehicles. Ethanol could be obtained from many sources including:

- starchy cereals and root crops (corn, wheat, potatoes)
- sugar-based feedstocks (sugarcane juice, molasses, sugar beet)
- cellulose (biomass: wood fibre, straw waste, bagasse).

There are many good reasons to use ethanol as a fuel or petrol-extender. These reasons include:

- Using a blend of 85% ethanol and 15% petrol (E85) will reduce net emissions of greenhouse gases by up to 37%. Lower blends (10% ethanol and 90% petrol) reduce greenhouse emissions by about 4%.
- Although ethanol burns with about 30% less energy (on a volume basis) than petrol, the presence of oxygen atoms in the ethanol molecule means that in a blend of 10% ethanol and 90% petrol (E10), the delivery of power to the engine is only 3% less than for unleaded petrol. The presence of the additional oxygen gives a cleaner and faster combustion. It also keeps the engine cooler.
- Ethanol fuel in modified engines does not produce solid, sooty deposits. Ethanol–petrol blends in normal engines also lead to the decrease in engine deposits.
- Toxic emissions of carbon monoxide are reduced when ethanol is used as a fuel.
- Blending ethanol with petrol helps to mitigate against petrol shortages.

It seems unlikely that a viable ethanol industry will be established in Australia in the near future. Although modern ethanol biofuel production plants are designed for zero water effluents, there is still the requirement for large amounts of processing water during production of the fuel. This is important in a dry continent such as Australia. As long as petrol remains cheaper, there is less impetus to develop the ethanol industry. In 2003 the Australian government legislated that ethanol–petrol blends no greater than E10 could be sold to the public for car fuel. This was prompted by public concerns over engine damage that could be caused by higher blends. At present, the ethanol fuel industry can survive only because of exemptions from fuel tax allowed by the Australian government. An independent cost/benefit analysis quoted by the Queensland canegrowers suggests that the benefits of ethanol to the government significantly outweigh the costs by at least \$40 million annually.

#### Questions

1. Explain why Henry Ford believed that ethanol was a logical fuel to power motor vehicles.
2. An ethanol–petrol blend is labelled as E15. Explain the meaning of this labelling code.
3. Identify environmental reasons for the use of ethanol instead of petrol.
4. Explain why ethanol is not likely to replace petrol as a fuel for motor vehicles in the near future in Australia.