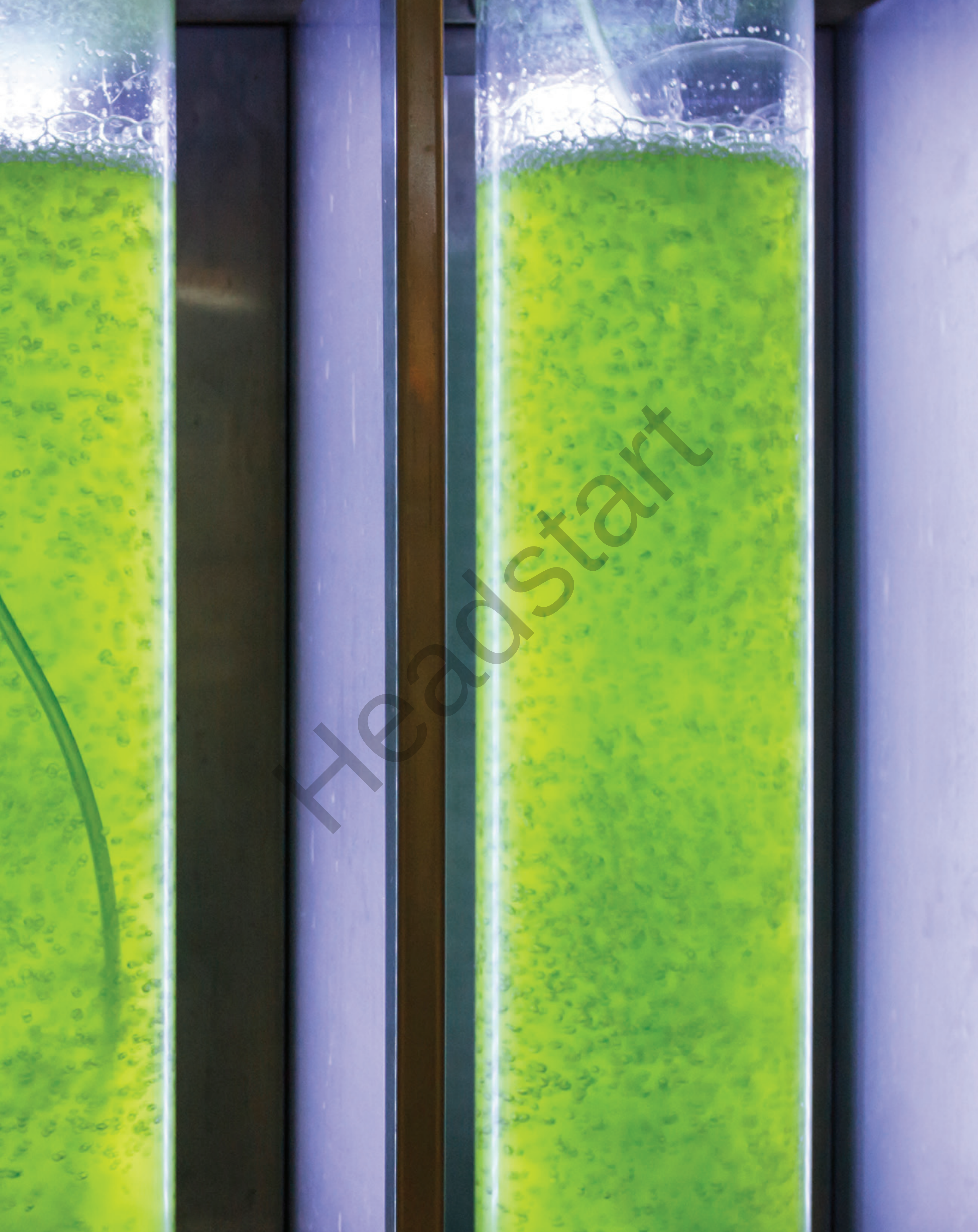

CHAPTER

02 Carbon-based fuels

In this chapter, you will learn how fuels are used to meet global energy needs and you will gain an appreciation of the chemistry that underpins decisions about the use of fuels. Combustion reactions are used to release useful heat energy from the chemical energy stored in fuels. You will consider different ways in which the energy content of a fuel is represented and be introduced to calculations involving energy changes. You will also learn about the energy changes occurring when the human body processes the food it consumes.

You will consider the environmental impact of using different types of fuels, as the phasing-out of fossil fuels is arguably the most significant factor in addressing climate change fears. Current research being conducted into the production of biofuels will also be discussed.

Key knowledge

- the definition of a fuel, including the distinction between fossil fuels (coal, natural gas, petrol) and biofuels (biogas, bioethanol, biodiesel) with reference to their renewability (ability of a resource to be replaced by natural processes within a relatively short period of time) **2.2**
- fuel sources for the body measured in kJ g^{-1}: carbohydrates, proteins and lipids (fats and oils) **2.3**
- photosynthesis as the process that converts light energy into chemical energy and as a source of glucose and oxygen for respiration in living things: $6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6O_2(g)$ **2.3**
- oxidation of glucose as the primary carbohydrate energy source, including the balanced equation for cellular respiration: $C_6H_{12}O_6(aq) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$ **2.3**
- production of bioethanol by the fermentation of glucose, $C_6H_{12}O_6(aq) \longrightarrow 2C_2H_5OH(l) + 2CO_2(g)$, and subsequent distillation to produce a more sustainable transport fuel **2.4**
- comparison of exothermic and endothermic reactions, with reference to bond making and bond breaking, including enthalpy changes (ΔH) measured in kJ, molar enthalpy changes measured in kJ mol^{-1} and enthalpy changes for mixtures measured in kJ g^{-1}, and their representations in energy profile diagrams **2.1**
- combustion (complete and incomplete) reactions of fuels as exothermic reactions: the writing of balanced thermochemical equations, including states, for the complete and incomplete combustion of organic molecules using experimental data and data tables. **2.5**

OA
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2.1 Exothermic and endothermic reactions

> A fuel is a substance that can release stored energy relatively easily.
> A combustion reaction is a reaction in which a substance reacts with oxygen gas, releasing energy.

Few issues are more relevant to modern society than energy. Our affluent lifestyle generates a huge demand for energy for electricity, heating and transport. The production of this energy, in turn, is placing serious stresses on our environment and climate. An understanding of energy involves an understanding that all chemicals contain stored energy and that any chemical reaction will produce an energy change. In this section, you will learn that fuels are substances that can release stored chemical energy relatively easily.

To release stored energy, fuels must react, often with oxygen. The reactions with oxygen are examples of **combustion** reactions. Reactions that release energy to the environment are called **exothermic** reactions, while reactions that absorb energy are **endothermic** reactions.

When **fuels** undergo combustion, energy is released in the form of heat. It is useful for chemists to be able to show the energy changes that occur as a reaction proceeds. All reactions absorb some energy before they can proceed, even if energy is released overall. An energy profile diagram represents the energy changes that occur during the course of a reaction.

ENTHALPY CHANGE

The **chemical energy** of a substance is sometimes called its **heat content** or **enthalpy**. It is given the symbol H. The enthalpy of the reactants in a chemical reaction is given the symbol H_r and the enthalpy of the products is given the symbol H_p.

Most chemical processes take place in open systems under a constant pressure (usually atmospheric). The exchange of heat energy between the system and its surroundings under constant pressure is referred to as the **enthalpy change**, or heat of reaction, and is given the symbol ΔH. The capital delta symbol (Δ) is commonly used in chemistry to represent 'change in'. For example, ΔT is the symbol for change in temperature.

> Enthalpy change is a measure of the quantity of energy absorbed or released during chemical reactions. It is given the symbol ΔH and is determined by subtracting the enthalpy of the reactants (H_r) from the enthalpy of the products (H_p).
> Enthalpy change, $\Delta H = H_p - H_r$

Fuels provide you with energy by undergoing exothermic combustion reactions. Knowing the precise enthalpy change per mole or gram that occurs during the combustion of different fuels helps you to decide which fuel might be most suitable for a particular purpose.

For the general reaction:

$$\text{reactants} \longrightarrow \text{products}$$

the enthalpy change (ΔH) is calculated by:

$$\Delta H = H_p - H_r$$

For reactions to occur, the bonds in the reactants must break and new bonds must be formed when the products are formed. It requires energy to break the bonds in the reactants and energy is released when bonds form in the products. The enthalpy of the products will differ from the enthalpy of the reactants. In some reactions, energy is released to the surroundings while in others, energy is absorbed from the surroundings.

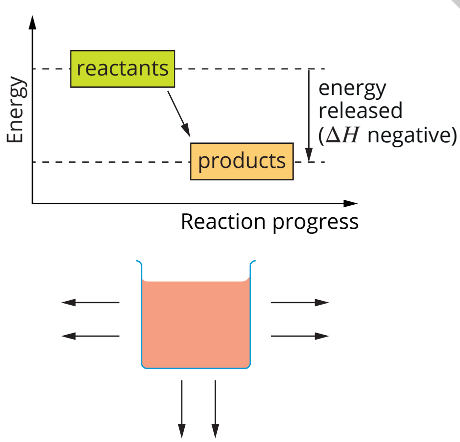


FIGURE 2.1.1 In an exothermic reaction, the energy of the reactants is greater than the energy of the products, so energy is released to the surroundings during the reaction and ΔH is negative.

Enthalpy change in exothermic reactions

When H_p is less than H_r, energy is released from the system into the surroundings, so the reaction is exothermic. The system has lost energy, so ΔH has a negative value.

Therefore, for combustion reactions (which are exothermic reactions), $\Delta H < 0$ (see Figure 2.1.1).

In an exothermic reaction:

- the total chemical energy of the products is less than the total chemical energy of the reactants
- the energy released when the bonds in the products form is greater than the energy required to break the bonds in the reactants

- excess energy is released to the surroundings
- ΔH is negative.

Enthalpy change in endothermic reactions

When H_p is greater than H_r, energy must be absorbed from the surroundings, so the reaction is endothermic. The system has gained energy, so ΔH has a positive value, i.e. $\Delta H > 0$ (see Figure 2.1.2).

In an endothermic reaction:

- the total chemical energy of the products is greater than the total chemical energy of the reactants
- the energy released when the bonds in the products form is less than the energy required to break the bonds in the reactants
- the energy required is absorbed from the surroundings
- ΔH is positive.

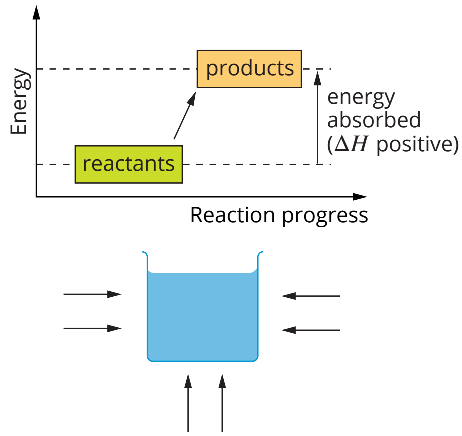


FIGURE 2.1.2 In an endothermic reaction, the energy of the reactants is less than the energy of the products, so energy is absorbed from the surroundings during the reaction and ΔH is positive.

Activation energy

The energy required to break the bonds of reactants so that a reaction can proceed is called the **activation energy**. The activation energy is an energy barrier that must be overcome before a reaction can commence.

An activation energy barrier exists for both exothermic and endothermic reactions. If the activation energy for a reaction is very low, the chemical reaction can be initiated as soon as the reactants come into contact because the reactants already have sufficient energy for a reaction to take place. Special conditions are not always required for reactions to occur. An example of this can be seen in the reaction between zinc and hydrochloric acid in Figure 2.1.3.

The reaction between zinc and hydrochloric acid produces hydrogen gas:

$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

As you can see in the figure, bubbles of hydrogen gas are vigorously produced as soon as zinc is added to the acid.

FIGURE 2.1.3 When zinc comes into contact with hydrochloric acid, it reacts almost immediately. The reactants have sufficient energy to 'overcome' the activation energy barrier.

Units of energy

It is useful to know the magnitude of ΔH values so that fuels can be compared. The international system of units (SI units) is a widely used system of measurement that specifies units for a range of quantities. The SI unit for energy is the **joule**, with the symbol J. As 1 J of energy is a relatively small quantity, it is common to see the following units in use.

- kilojoules, 1 kJ = 10^3 J
- megajoules, 1 MJ = 10^6 J
- gigajoules, 1 GJ = 10^9 J
- terajoules, 1 TJ = 10^{12} J.

Figure 2.1.4 provides a conversion guide for different energy units.

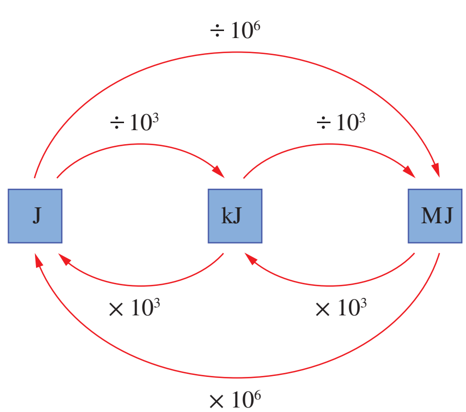


FIGURE 2.1.4 Converting between different energy units

Writing a thermochemical equation

The combustion reaction for the fuel methane is:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

Activation energy is required to break the covalent bonds in both methane and oxygen molecules for this reaction to proceed. Methane is a widely used fuel as the energy released when bonds form in CO_2 and H_2O is significantly higher than the activation energy required.

The quantity of energy released in the combustion of one mole of methane is 890 kJ. If the value of ΔH is added to a balanced equation, it is referred to as a **thermochemical equation**. The thermochemical equation for the combustion of methane is:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890 \text{ kJ}$$

This equation tells you that the combustion of 1 mole of methane and 2 moles of oxygen gas to produce 1 mole of carbon dioxide and 2 moles of liquid water will release 890 kJ of energy.

A thermochemical equation is a balanced chemical equation that includes the enthalpy change, ΔH.

ENERGY PROFILE DIAGRAMS

The energy changes that occur during the course of a chemical reaction can be shown on an **energy profile diagram** or energy profile.

The energy profile diagram for an exothermic reaction like the one shown in Figure 2.1.5 indicates that the enthalpy of the products is less than the enthalpy of the reactants. Overall, energy is released and so the ΔH value is negative. The energy profile also shows that, even in exothermic reactions, activation energy must first be absorbed to start the reaction.

The energy profile diagram for an endothermic reaction (Figure 2.1.6) shows that the enthalpy of the products is greater than the enthalpy of the reactants. Overall, energy is absorbed and so the ΔH value is positive. The energy profile also shows the absorption of the activation energy before the release of energy as bonds form in the products.

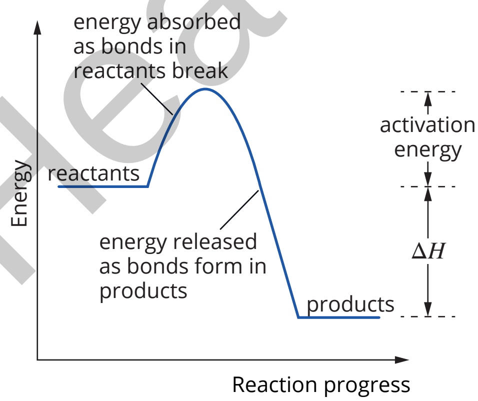


FIGURE 2.1.5 The characteristic shape of an energy profile diagram for an exothermic reaction

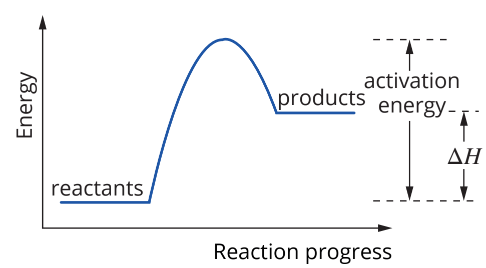


FIGURE 2.1.6 The characteristic shape of an energy profile diagram for an endothermic reaction

2.1 Review

SUMMARY

- A fuel is a substance with stored energy that can be released relatively easily for use as heat or power.
- All chemical reactions involve a change in energy due to the breaking of reactant bonds and the formation of new bonds.
- The chemical energy of a substance is sometimes called its heat content or enthalpy.
- The net enthalpy change in a reaction is represented as ΔH.
- Exothermic reactions have a net release of energy to the surroundings. ΔH is negative.
- Endothermic reactions have a net absorption of energy from the surroundings. ΔH is positive.
- The combustion of fuels is an exothermic process.
- Energy profile diagrams are used to represent the energy changes in a reaction.

KEY QUESTIONS

Knowledge and understanding

1 Which one of the following is a correct thermochemical equation for the combustion of methane?

A $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

B $CH_4(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$ $\Delta H = -890$ kJ

C $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ $\Delta H = -890$ kJ

D $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ $\Delta H = +890$ kJ

2 Complete the following sentences by selecting the correct term for each of the alternatives in bold:
In an exothermic reaction, the chemical potential of the **products/reactants** is lower than that of the **products/reactants.** Energy is **absorbed from/ released to** the surroundings. The sign of ΔH will be **positive/negative.**

3 Explain what a negative ΔH value indicates about a chemical reaction, in terms of the relative enthalpies of the reactants and products.

4 Explain why both exothermic and endothermic reactions require activation energy to proceed.

5 Use Figure 2.1.4 to convert each of the following to kJ.

a 25.8 J

b 26.3 MJ

c 6.6 GJ

Analysis

6 Ammonium chloride, NH_4Cl, is readily soluble in water. The reaction with water is endothermic and can be represented by the equation:

$$NH_4Cl(s) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

5.0 g of NH_4Cl is added to water and stirred until it dissolves.

a What bonds need to be broken for this reaction to occur?

b Will this reaction absorb or release energy to the environment?

c Will the temperature of the surroundings increase or decrease when this reaction occurs?

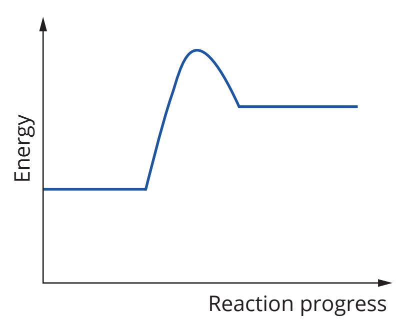
7 The energy profile diagram below shows the energy changes during the reaction of hydrogen and iodine to form hydrogen iodide:

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

a Is the reaction exothermic or endothermic?

b Describe how the enthalpies of the reactants and products compare to one another.

c Comment on the size of the activation energy compared with ΔH.



2.2 Types of fuels

FIGURE 2.2.1 Sugars, such as sucrose, are fuels for your body.

FIGURE 2.2.2 Petrol is just one type of fuel that is used each day to meet our energy needs.

Fuels provide you with energy. They are substances that have chemical energy stored within them. All chemicals contain stored energy. What makes a fuel special is that this stored chemical energy can be released relatively easily.

Sugar is an example of a common fuel (Figure 2.2.1). A cube of table sugar (sucrose) can provide your body with 82 kilojoules of energy. This is about 1% of your daily energy needs. If sucrose is burnt, this energy is released as heat. The combustion of 1 kilogram of sucrose releases sufficient energy to melt more than 5 kilograms of ice and then boil all the liquid water produced.

Although sugars provide energy for your body, you do not heat your home, power cars or produce electricity by burning sugar. A range of other fuels such as wood, coal, oil, natural gas, LPG, ethanol and petrol (Figure 2.2.2) are used for these energy needs.

In this section, you will explore the range of fuels available and how they are sourced.

THE NEED FOR FUELS

A fuel is a substance with stored energy that can be released relatively easily for use as heat or power. Although this chapter will focus on fuels with stored chemical energy, the term ‘fuel’ is also applied to sources of nuclear energy, such as uranium.

The use of fuels by society can be considered from a number of points of view, including at a:

- local level (e.g. the type of petrol used in your car)
- national level (e.g. whether Australia’s use of energy resources is **sustainable**)
- global level (e.g. whether the use of **fossil fuels**—coal, oil and natural gas—is contributing to the enhanced greenhouse effect).

These are not separate issues. Choices made locally have regional and global effects. The decisions of global and national governments affect how and which fuels are used.

Use of energy in Australia and the world

World energy consumption is around 4×10^{20} joules per year. The United States consumes a quarter of the world’s energy. Australia consumes about 1% of the world’s energy. But energy consumption per person in Australia is only just below that of the United States. Figure 2.2.3 shows the ways in which Australians use energy. As you can see, heating and transportation account for 87% of Australia’s total energy consumption.

In Australia and around the world, most of the energy used for heating, electricity generation and powering vehicles comes from fossil fuels. In 2021, approximately 70% of Australian electricity was generated from these fuels, with around 50% from coal and the remainder from natural gas and oil. The other approximately 30% of Australia’s electricity came from renewable energy sources. Hydroelectricity contributed 6% of total electricity, and wind, biofuels and solar energy made up the remaining 24%.

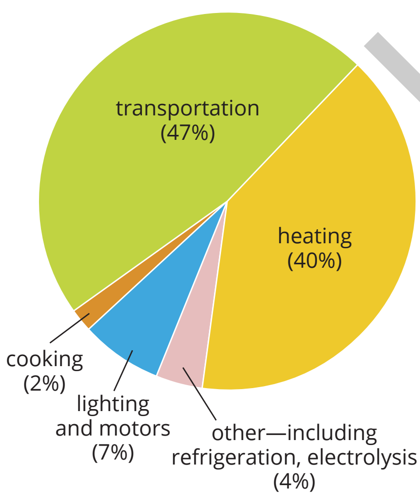


FIGURE 2.2.3 This pie chart shows where energy is used in Australia.

Future energy needs

World energy supply is in a state of flux and change. For most of the twentieth century, world energy consumption grew exponentially, and the coal and oil industry expanded to meet this demand. Over the last decades, however, it has become apparent that reserves of fossil fuels are finite and that the emissions from fossil fuels are threatening climate stability.

Given the limited reserves and concerns about the link between fossil fuels and climate change, there is considerable interest in identifying and developing new energy sources. Most countries are managing a transition to alternative sources of energy, but the use of **renewable fuels** (also known as **renewables**), fuels that can be replaced at a sustainable rate, for large-scale energy production is not a simple task. Replacement energy sources need to meet a range of requirements, such as being reliable, sustainable and cost-effective. Figure 2.2.4 provides a breakdown of how the world's energy is currently sourced.

> Fuels are considered to be renewable if they can be replaced at a sustainable rate.
> Non-renewable fuels are fuels that are consumed at a faster rate than they can be replaced.

World consumption
Million tonnes oil equivalent

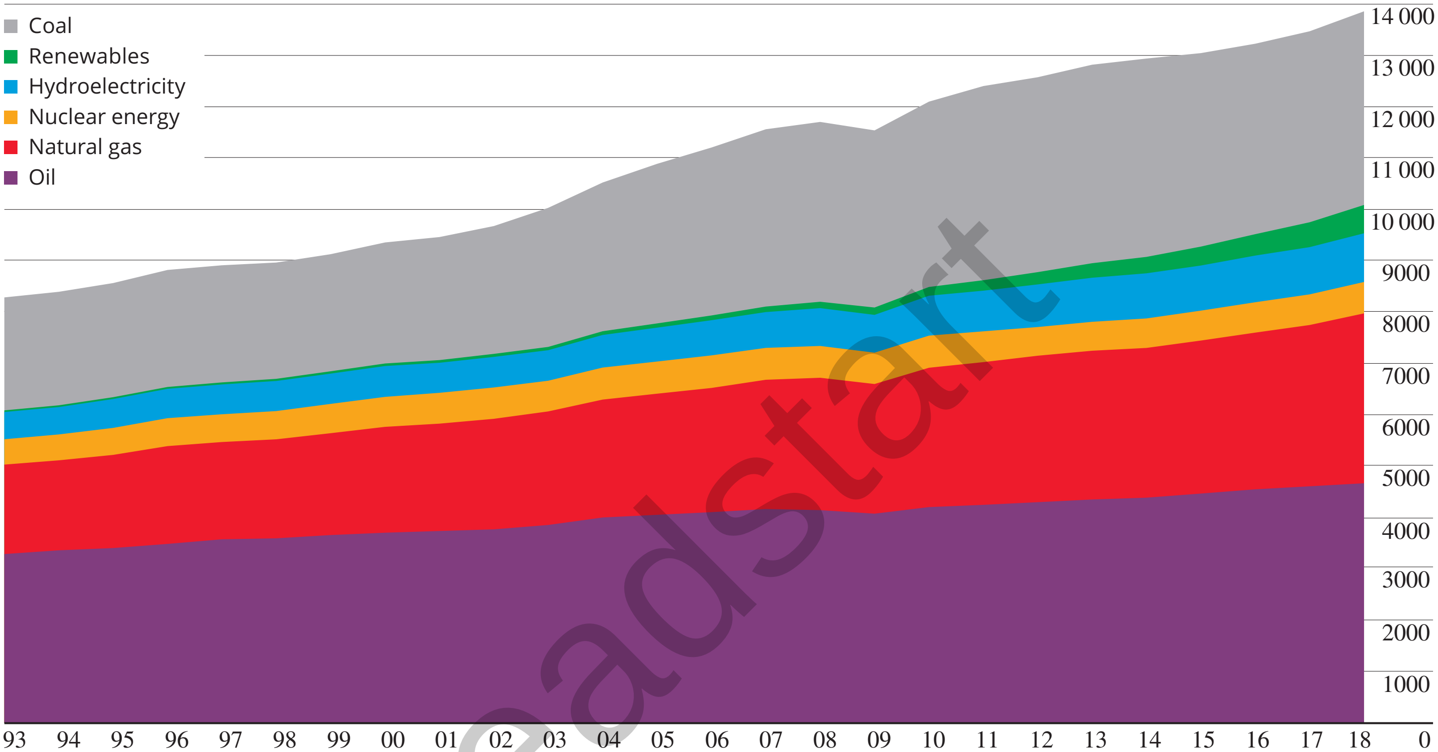


FIGURE 2.2.4 As the world's energy requirements have grown, renewable energy sources have provided an increasing, but still small, proportion of our overall energy usage.

FOSSIL FUELS

Non-renewable resources are those that are used faster than they can be replaced. Coal, oil and natural gas are non-renewable fuels. Reserves of fossil fuels are limited and they could eventually be exhausted.

> Fossil fuels are naturally occurring fuels such as coal, oil or gas, that were formed in the geological past from the remains of living organisms.

Formation of fossil fuels

Coal, oil and natural gas were formed from ancient plants, animals and microorganisms. Buried under tonnes of mud, sand and rock, this once biological material has undergone complex changes to become the fossil fuels used by societies today. The organic matter still retains some of the chemical energy the plants originally accumulated by carrying out **photosynthesis**. Chemical energy in fossil fuels can be considered to be trapped solar energy.

Fossil fuel formation occurs over millions of years. This is why these fuels are considered non-renewable. Once reserves of the fossil fuels have been used, they will not be replaced in the foreseeable future.

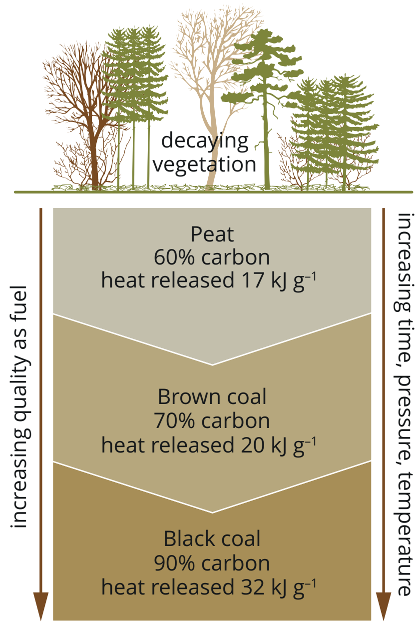


FIGURE 2.2.5 Steps in the formation of coal. Values of the carbon content and heat released upon combustion are for dried coal.

Coal

As wood and other plant material is converted into coal, the carbon content increases and the proportion of hydrogen and oxygen decreases. The wood progressively becomes peat, brown coal and then black coal (see Figure 2.2.5). Coal is a mixture of large molecules made from carbon, hydrogen, nitrogen, sulfur and other elements.

Electricity from coal

Chemical energy from most fuels is harnessed through combustion of the fuel. Thermal energy released from the combustion of fuels can be converted into electrical energy. In Australia, electrical energy is produced from several different fuels.

The combustion of coal generates over 50% of Australia's electricity. Rather than transport coal to every factory, office and household, the chemical energy is converted to electrical energy at a power station. Electricity is transmitted easily from the power station by metal cables and wires to other regions. The reaction occurring when coal burns can be written as:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

The energy released from the combustion of coal is about 32 kJ g^{-1}.

Figure 2.2.6 illustrates how thermal energy is released when the coal is converted to electrical energy.

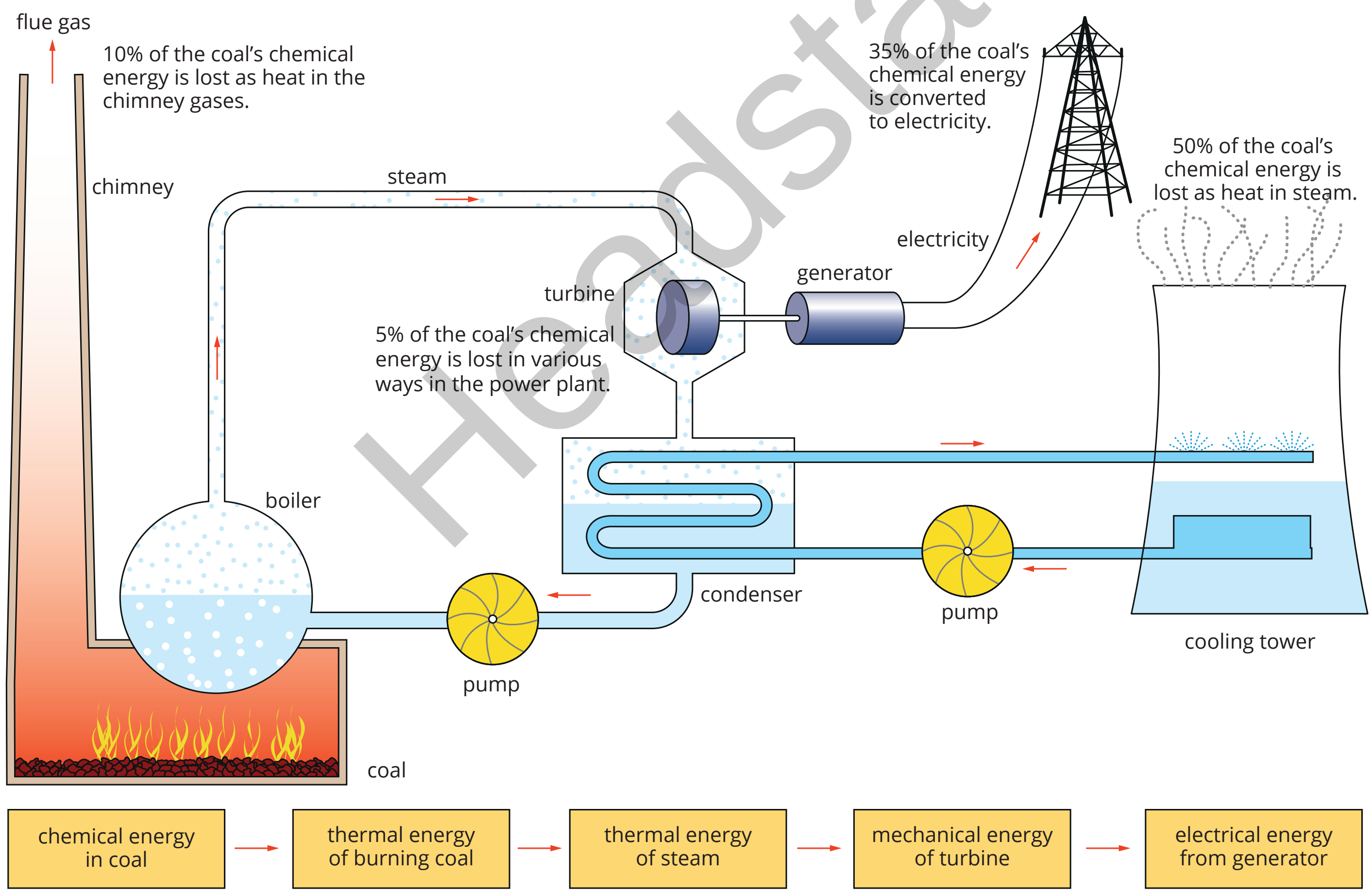


FIGURE 2.2.6 A representation of the process of burning coal to produce electricity. The chemical energy in the coal undergoes several transformations before electricity is produced.

Most Australian states are trying to retire their large-scale coal-fired electricity plants ahead of schedule in response to concerns about their greenhouse emissions. For example, the Hazelwood power station that had been producing around 20% of Victoria's electricity was closed in 2017.

Petrol

Crude oil (petroleum) is a mixture of **hydrocarbon** molecules that are mostly members of the **homologous series** of **alkanes**. Crude oil itself is of no use as a fuel, but it contains many useful compounds. These useful compounds are separated into a range of fractions by **fractional distillation**. Fractional distillation does not produce pure substances. Each fraction is still a mixture of hydrocarbon compounds. These fractions can be used as fuels or treated further to produce more specific products through chemical processes.

Petrol is one of the fractions obtained from crude oil. It includes the compound octane and other alkanes with a similar boiling point. The equation for the combustion of octane is:

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$$

Combustion occurs in the cylinder of a car engine. The hot gases formed push the piston in the engine, enabling the car to move.

Diesel, or more correctly, **petrodiesel**, is also a fraction of crude oil. The alkanes in petrodiesel are slightly longer molecules than those in petrol.

Natural gas

Natural gas is another fossil fuel found in deposits in the Earth's crust. It is mainly composed of methane (CH_4) together with small amounts of other hydrocarbons such as ethane (C_2H_6) and propane (C_3H_8). Water, sulfur, carbon dioxide and nitrogen may also be present in natural gas.

Natural gas can be found:

- in gas reservoirs trapped between layers of rocks
- as a component of petroleum deposits
- in coal deposits where it is bonded to the surface of the coal.

Coal seams usually contain water and the pressure of the water can keep the gas adsorbed to the coal surface. Natural gas found this way is known as coal seam gas or CSG. It is a major component of the energy supplies of Queensland.

Natural gas is accessed by drilling as with crude oil; drilling allows the natural gas to flow to the surface (see Figure 2.2.7).

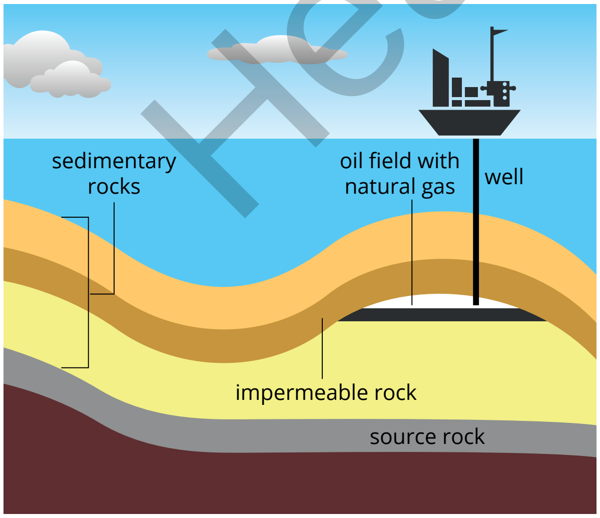


FIGURE 2.2.7 Natural gas deposits are often found trapped above crude oil. Once a well is sunk into the deposit, the natural gas flows to the surface.

In 2018 Australia replaced Qatar as the world's leading exporter of natural gas. In November 2018 alone, Australia exported 6.5 million tonnes of natural gas. Natural gas is exported as a liquid, referred to as LNG. The conversion to a liquid increases the energy density but the liquification consumes a significant quantity of energy.

Electricity from natural gas

Natural gas is used in Victoria to generate electricity for the power grid. In a gas-fired power plant, methane and other small alkanes are burnt to release energy. As shown in Figure 2.2.8, the hot gases produced by combustion cause air to expand in a combustion turbine to generate electrical energy. This is a simpler process than in a coal-fired plant where the thermal energy is used to produce steam.

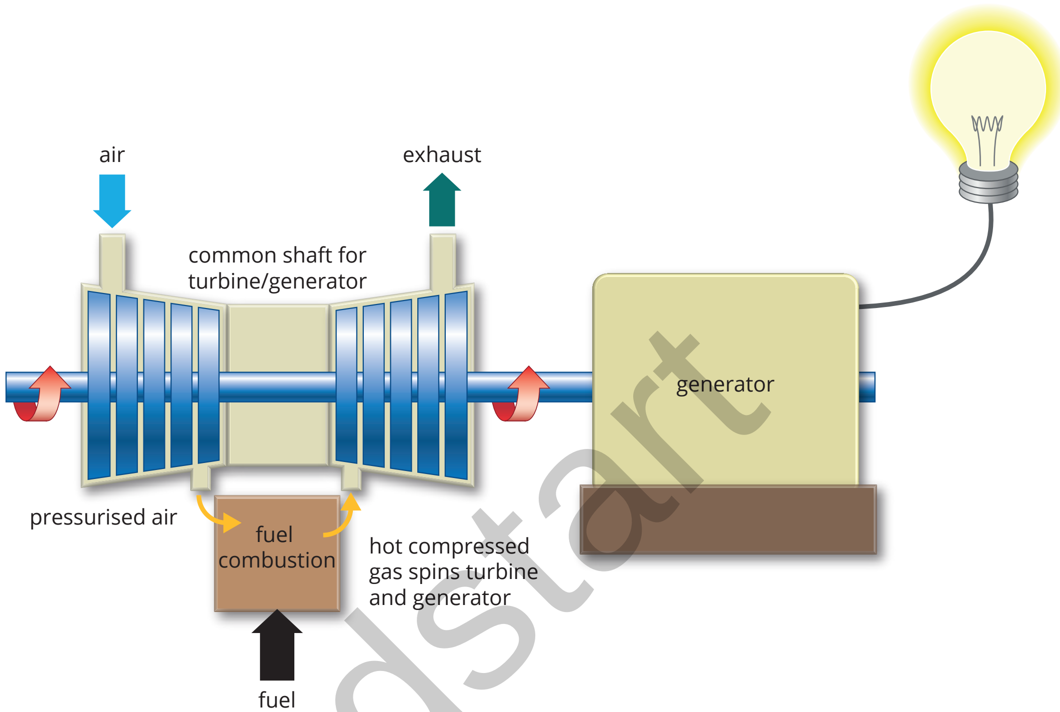


FIGURE 2.2.8 In a gas-fired power plant, the hot gases produced expand air in a combustion turbine to generate electricity.

FIGURE 2.2.9 Many homes use natural gas for cooking and/or heating.

The composition of natural gas varies but the main combustion reaction involves methane. The equation is:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Natural gas has many domestic applications. A network of pipes is used to deliver natural gas to most cities in Victoria where it is used for cooking (Figure 2.2.9), hot water and home heating.

BIOFUELS

Governments and industry are exploring alternatives to fossil fuels to meet our future energy needs and limit the impact of fossil fuels on the environment. Ideally, new sources of energy will be renewable. Renewable energy is energy that can be obtained from natural resources that can be constantly replenished.

Biochemical fuels (or **biofuels**) are fuels derived from plant materials such as grains (maize, wheat, barley or sorghum), sugar cane (Figure 2.2.10 on the following page) and vegetable waste, and vegetable oils. The three main biofuels are **bioethanol**, **biogas** and **biodiesel**. They can be used alone or blended with fossil fuels such as petrol and diesel. Bioethanol will be discussed in detail in Section 2.4.

> Biofuels are fuels derived from plants or animals. They can usually be replenished at a sustainable rate, hence are considered forms of renewable energy.

FIGURE 2.2.10 Harvesting sugar cane in Queensland. Sugar cane can be a source of the raw materials for the production of bioethanol.

As well as being renewable, biofuels are predicted to have less impact on the environment than fossil fuels. The plant materials used in the generation of biofuels are produced by photosynthesis, which removes carbon dioxide from the atmosphere and produces glucose ($C_6H_{12}O_6$) in the following reaction:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$

The plants convert the glucose into **cellulose** and starch. Although carbon dioxide is released back into the atmosphere when the biofuel is burnt, the net impact should be less than for fossil fuels. In theory a biofuel could be **carbon neutral**, absorbing the same amount of CO_2 in its formation as is released in its combustion. In practice, energy is required to farm, fertilise and transport biofuels, so they are not likely to be fully carbon neutral.

Biogas

Biogas is gas that is released in the breakdown of organic waste by **anaerobic** bacteria. These bacteria decompose the complex molecules contained in substances such as carbohydrates and proteins into the simple molecular compounds carbon dioxide and methane. A digester (Figure 2.2.11) is a large tank filled with the anaerobic bacteria that digest (consume) the complex molecules to form biogas.

CHEMFILE

Berrybank piggery biogas

Berrybank Farm near Ballarat is an example of the innovative use of biogas. Over $2 million has been spent on building infrastructure to collect the manure from 20 000 pigs. The manure is fed into a digester, shown in the figure below, that produces two useful products: biogas and fertiliser. The biogas is used to fire generators that produce an estimated $250 000 of electricity annually. Some of the energy produced is used to maintain the temperature of the biodigester above 30°C—not always easy in a Ballarat winter.

The large digestor tanks used at the piggery for biogas production

There are now several Victorian farms that have installed biodigesters, but the Berrybank operation was the first; it was established over 30 years ago. The cost at that time was around 2 million dollars but the savings in electricity and water consumption have ensured the venture is profitable.

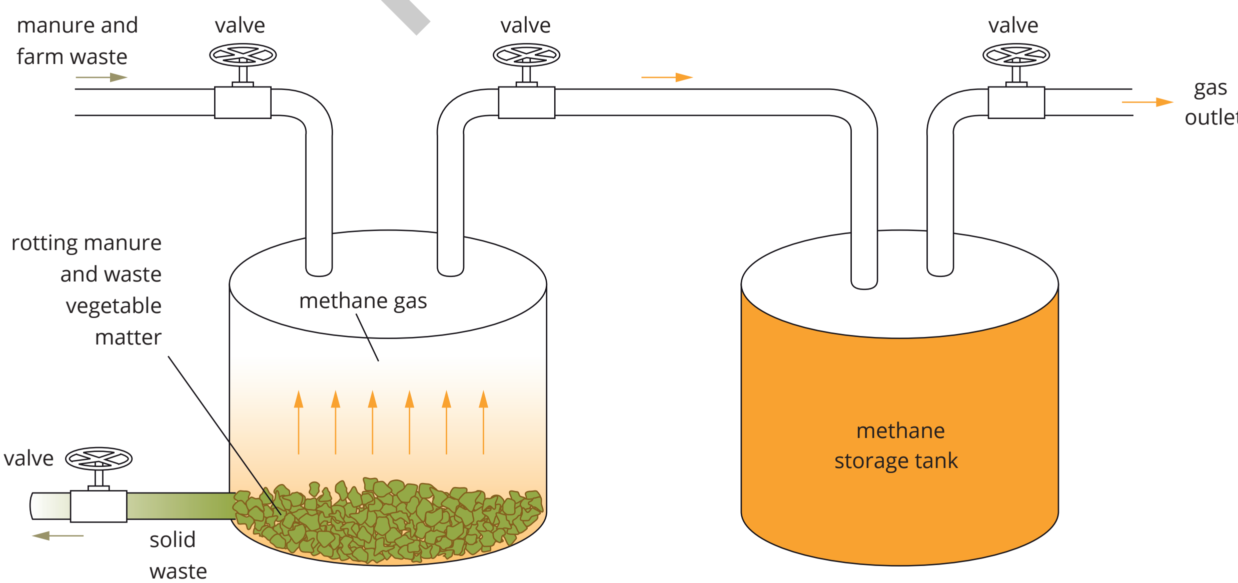


FIGURE 2.2.11 A digester is used in the production of biogas.

Biogas is formed in anaerobic conditions by the action of bacteria. The main component of biogas that acts as a fuel is methane.

TABLE 2.2.1 Typical percentage composition of different gases found in biogas

Gas	Formula	Percentage composition (by volume)
methane	CH_4	60
carbon dioxide	CO_2	32
nitrogen	N_2	4.5
hydrogen sulfide	H_2S	2
oxygen	O_2	1
hydrogen	H_2	0.5

FIGURE 2.2.12 Pipes buried in this rubbish tip collect biogas.

A range of materials, including rotting rubbish and decomposing plant material, can be used to produce biogas.

The composition of biogas depends on the original material from which it is obtained and the method of decomposition. The typical composition of a sample of biogas is shown in Table 2.2.1.

As you can see from Table 2.2.1, biogas consists mainly of methane and carbon dioxide. Biogas can be used for heating and to power homes and farms. There are more than 30 million biogas generators in China. Biogas generators are particularly suited to farms, as the waste from a biogas generator makes a rich fertiliser.

In the future, it is likely more energy will be obtained from biogas generated at sewage works, chicken farms, piggeries and food-processing plants. Your local rubbish tip also has the potential to supply biogas (see Figure 2.2.12). The gas can be used directly for small-scale heating or to generate electricity.

Electricity from biogas

Biogas can be used to generate electricity, usually in small-scale electricity generators rather than large power plants. These smaller generators are often located at the site where the biogas is produced. For example, sewage works commonly burn biogas produced in a generator to supply some of their power needs.

The main reaction occurring in the combustion of biogas is the same reaction as that of a gas-fired power station, the combustion of methane. The energy released per gram of biogas is less than that of natural gas because the methane content in biogas is significantly lower.

Biodiesel

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

The usual raw material for the production of biodiesel is vegetable oil from sources such as soybean, canola or palm oil. Recycled vegetable oil or animal fats can also be used. Fats and oils are **triglycerides** with a molecular structure consisting of three hydrocarbon chains, each attached by an ester functional group to a backbone of three carbon atoms, as shown in Figure 2.2.13. The triglyceride is converted into biodiesel by warming it with an alcohol, usually methanol or ethanol, in a process known as **transesterification**. Concentrated KOH is used as a **catalyst** in the reaction.

In the transesterification reaction, the triglyceride is converted into a small molecule called glycerol and three ester molecules with long carbon chains. The ester molecules are the biodiesel product. This biodiesel can be used as the fuel for some diesel engines.

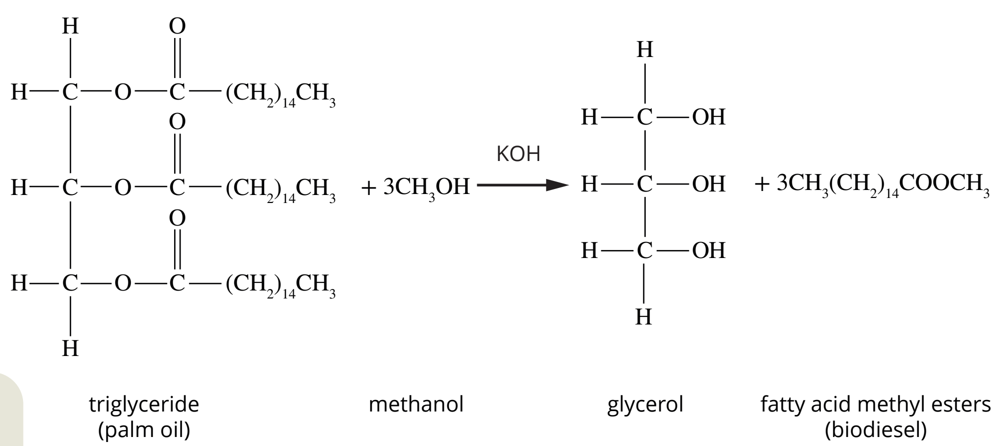


FIGURE 2.2.13 The reaction of a triglyceride with methanol and a KOH catalyst to form fatty acid methyl esters (biodiesel) and glycerol

Biodiesel molecules are esters of fatty acids, formed from the reaction between triglycerides and small alcohol molecules.

The structure of a typical biodiesel molecule is shown in Figure 2.2.14.

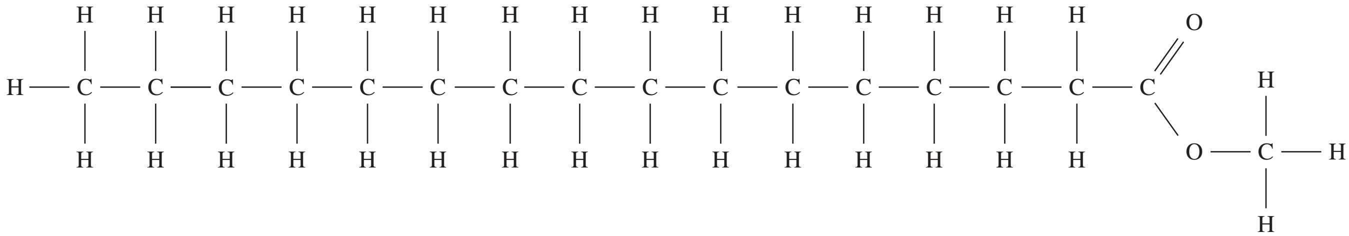


FIGURE 2.2.14 Structural formula of a typical biodiesel molecule

RENEWABILITY

Fossil fuels are a non-renewable source of energy. It took millions of years for their formation in the Earth's crust, so the likelihood of new deposits forming cannot be considered.

Biofuels are renewable and current production levels are sustainable. However, currently biofuels produce only a small percentage of Australia's fuel needs. For biofuel production to increase significantly, we would need to grow crops specifically for this purpose. This would present a number of issues, including land degradation, clearing of forest and bushland, and ensuring food supplies are maintained.

It is mainly wind and solar investments that are steadily replacing fossil fuels. Figure 2.2.15 from the Australian Clean Energy Council shows that in 2021, renewables accounted for over 32% of our electricity generation and this figure is increasing each year.

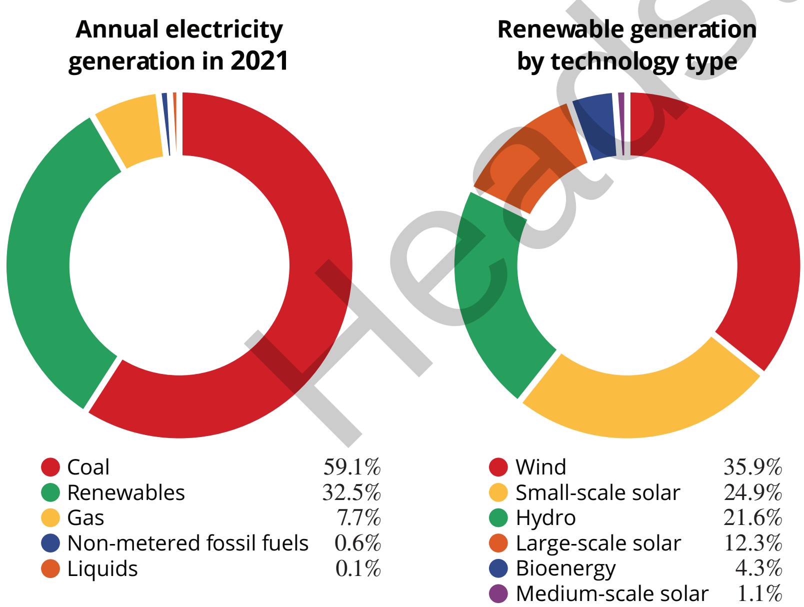


FIGURE 2.2.15 A 2021 breakdown of how Australia's electrical energy is sourced

It is also interesting to see in Figure 2.2.16, the divergent paths of various Australian states in their energy production. Tasmania produced nearly all of its energy in 2021 from renewable sources, while Queensland and New South Wales were below 30%.

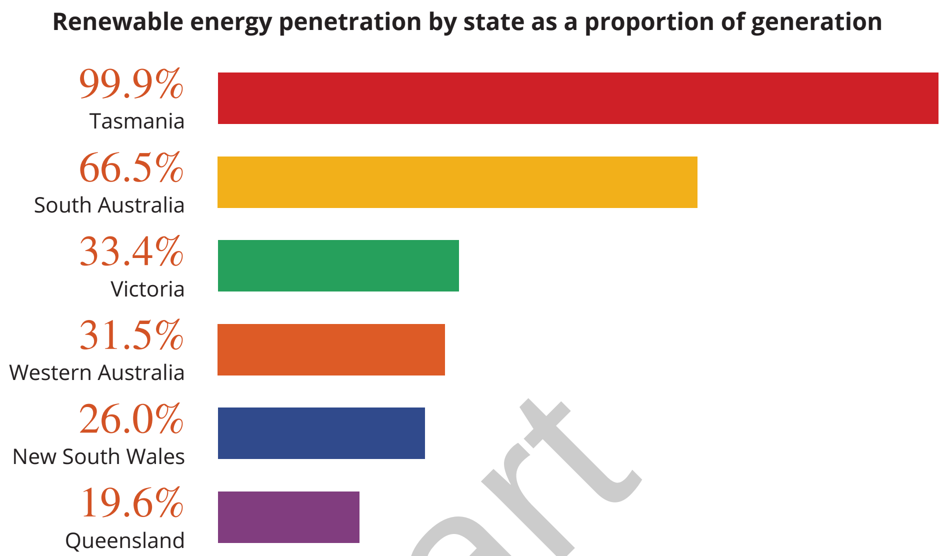


FIGURE 2.2.16 The level of renewable energy use varies significantly between the Australian states.

Table 2.2.2 compares the advantages and disadvantages of some fuels.

TABLE 2.2.2 Advantages and disadvantages of fuels described in this section

Fuel	Advantages	Disadvantages
Coal	• Large reserves • Less easily transported than liquid or gaseous fuels • Relatively high energy content	• Non-renewable • High level of emissions
Natural gas	• More efficient than coal for electricity production • Easy to transport through pipes • Relatively high energy content	• Non-renewable • Limited reserves • Polluting but less than coal and petrol
Biogas	• Renewable • Made from waste • Reduces waste disposal • Low running costs • CO_2 absorbed during photosynthesis	• Low energy content • Supply of waste raw materials limited
Petrol	• High energy content • Ease of transport	• Non-renewable • Polluting but less than coal • Limited reserves
Bioethanol	• Renewable • Can be made from waste • CO_2 absorbed during photosynthesis • Burns smoothly • Fewer particulates produced than petrol	• Limited supply of raw materials from which to produce it • Lower energy content than petrol • May require use of farmland otherwise used for food production

2.2 Review

OA ✓✓

SUMMARY

- A fuel is considered to be non-renewable if it cannot be replenished at the rate at which it is consumed. Fossil fuels such as coal, oil and natural gas are non-renewable.
- Fuels such as petrol, natural gas and petrodiesel undergo combustion reactions in excess oxygen to form carbon dioxide and water.
- The combustion reactions of fuels are used to produce electricity and to power vehicles.
- Fuels are considered to be renewable if they can be replenished at a sustainable rate.
- Biogas is formed by the anaerobic breakdown of organic waste. It is usually burnt to generate electrical energy.
- Biodiesel is produced from triglycerides in animal fats or plant oils. The triglycerides react with methanol in a transesterification reaction to form biodiesel.
- Some of the non-renewable and renewable fuels in use in Australia:

Non-renewable fuels	Renewable fuels
coal oil, petrol, petrodiesel natural gas	bioethanol biogas biodiesel

- Biofuels offer several environmental advantages: CO_2 is absorbed during the growth of crops used in their production, they can be replenished, and they can be produced from material that would otherwise have been waste.
- A shift to large-scale production of biofuels could place a strain on resources and available farmland.

KEY QUESTIONS

Knowledge and understanding

1 Use natural gas as an example to explain what a fuel is.

2 What is the difference between a renewable and non-renewable fuel?

3 A large dairy farm in country Victoria has built a digestor to process the cow manure.

a Which biofuel would be produced from the animal waste?

b How is this fuel most likely to be used?

4 There are several small plants in Australia that collect the waste oil from businesses such as fish-and-chip shops.

a Which biofuel is produced from the waste oil?

b How is this fuel most likely to be used?

Analysis

5 Biodiesel and petrodiesel can both be used as a fuel for trucks. The two main products of combustion of these fuels are carbon dioxide and water. Explain why biodiesel is considered more sustainable than petrodiesel, even though the products of combustion are very similar.

6 The production of biogas from animal waste provides a fuel from a renewable source and disposes of a nuisance material. Despite the obvious benefits of biogas production, the volume used in Australia is still relatively low. Suggest reasons for this limited use.

7 Despite the fact that biodiesel can be produced from a renewable resource such as canola crops, there are still concerns with the production and use of biodiesel. Discuss what these concerns might be.

2.3 Fuel sources for the body

In Section 2.2 you learnt about the various fuels developed by humans for their external energy needs. In this section, you will focus on the energy needs of the body's internal processes. Humans require energy for warmth, movement and for the synthesis of necessary biomolecules such as hormones, enzymes, carbohydrates and triglycerides.

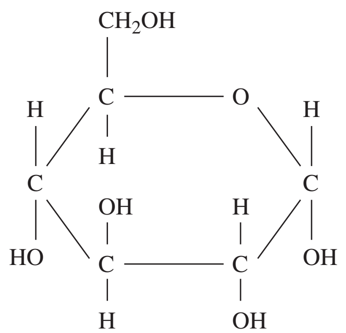


FIGURE 2.3.1 Structural formula of glucose

FIGURE 2.3.2 Green plants carry out photosynthesis during the day. Photosynthesis occurs in the leaves of the plant.

PHOTOSYNTHESIS

One of the most important biomolecules is glucose, shown in Figure 2.3.1.

Glucose is found in all living things, especially in the sap of plants and the blood and tissue of animals. Plants can use glucose as a monomer to form important natural polymers such as starch and cellulose. Both glucose and its polymer, starch, are more rapidly digested than other forms of food. They are the main sources of energy in most diets and the human body uses them for energy in preference to fats and proteins.

Green plants such as the one seen in Figure 2.3.2 carry out photosynthesis, one of the key chemical reactions that supports life. Plants use photosynthesis to make their own food in the form of glucose. Photosynthesis is an endothermic chemical reaction carried out in chloroplasts in the cells of green leaves. Energy from sunlight is used to produce glucose from carbon dioxide and water. Oxygen gas is the other product.

Glucose contains chemical energy which feeds the plant and is also stored and becomes food for animals that eat it.

The thermochemical equation for photosynthesis is shown below.

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6O_2(g) \qquad \Delta H = +2803 \text{ kJ}$$

CELLULAR RESPIRATION

Glucose is the primary energy source for the cells of plants and animals and is used to obtain energy by a process known as **cellular respiration**. The main form of respiration is also referred to as aerobic respiration as oxygen gas is required.

In aerobic respiration, glucose is oxidised to carbon dioxide and water through a sequence of reactions. The overall equation is:

$$C_6H_{12}O_6(aq) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H = -2803 \text{ kJ}$$

Note that the products of photosynthesis are the reactants for aerobic respiration. Figure 2.3.3 shows that the energy from the Sun stored in glucose molecules is released to the plant or animal through respiration. It should also be apparent that the respiration reaction is the same as the reaction that would occur if glucose were to undergo complete combustion in a flame. The glucose stores energy from the Sun as chemical energy.

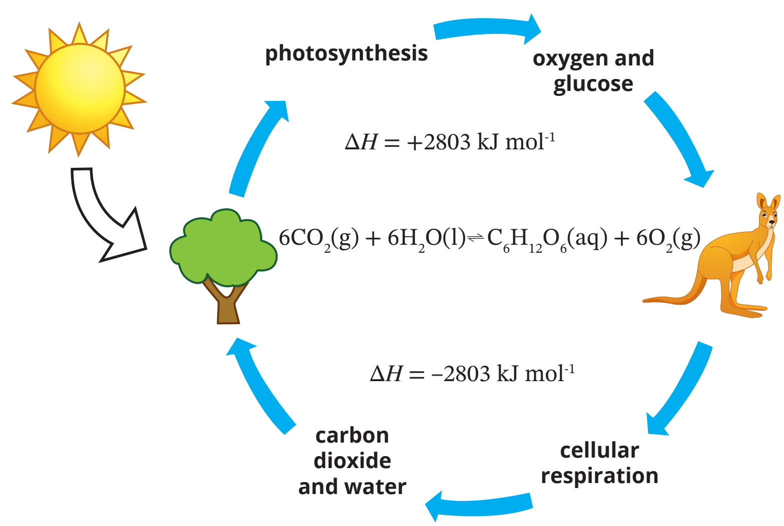


FIGURE 2.3.3 Photosynthesis in plants can store energy from the Sun in plants. Respiration of glucose releases that energy for the plant or animal to use.

Although the equations for photosynthesis and respiration are the reverse of each other, the actual processes are very different. Both reactions occur in stages, requiring the presence of a range of other biomolecules. Photosynthesis occurs in plant cells, while respiration in animals occurs in muscle cells.

> The thermochemical equations for photosynthesis and cellular respiration are:
>
> photosynthesis $6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6O_2(g)$ $\Delta H = +2803$ kJ
>
> respiration $C_6H_{12}O_6(aq) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$ $\Delta H = -2803$ kJ

CASE STUDY ANALYSIS

Lavoisier and combustion

Antoine Lavoisier was a famous French chemist. He published a systematic way of naming chemicals based on their composition, he discovered the composition of water, and he clarified the role of oxygen in combustion and oxidation, among his many achievements. From the early 1780s Lavoisier proposed that combustion and respiration were the same thing; that all respiration is a form of combustion. Given that oxygen had only recently been discovered, this was quite an amazing insight.

To test his theory, he designed an apparatus that included both a living guinea pig and ice. The vigorousness of the movement of the guinea pig gave an indication of the oxygen content of the air and the rate of melting of the ice provided a measure of the energy released. His experiments confirmed that respiration was a reaction used by the body to release energy.

Lavoisier next measured the volume of oxygen inhaled by a human volunteer, and he demonstrated that the volume increased with the rate of exercise. The volunteer's heart rate and pulse rate also increased. Figure 2.3.4 shows a sketch made by Lavoisier's wife Marie-Anne Lavoisier of this experiment. The volunteer can be seen sitting near the table and the apparatus to measure the air volume is on the table. A translation of Lavoisier's insightful conclusion reads:

Respiration is nothing but a slow combustion of carbon and hydrogen, similar in all respects to that of a lamp or a lighted candle, and from this point of view, animals which breathe are really combustible substances burning and consuming themselves.

One of Lavoisier's conclusions, referring to the location of respiration, did have to be modified about 100 years later. Lavoisier assumed incorrectly that it was in the lungs themselves rather than in body cells.

FIGURE 2.3.4 Lavoisier's experiment to measure the oxygen intake and energy output of a volunteer

Analysis

1 Lavoisier wanted to show that respiration and combustion of glucose are the same thing. Use an equation to explain what this means.

2 Lavoisier used ice in his apparatus as an indicator of how much heat his volunteer generated. Explain how ice could be used to do this.

3 Lavoisier used a live guinea pig as an indication of air quality. Explain how the behaviour of the guinea pig could indicate air quality.

4 Discuss some of the variables Lavoisier might have considered monitoring in his investigation of the respiration process of a volunteer.

> One of the main reasons humans consume nutrients is to obtain energy. The quantity of energy obtained depends upon the bonding in the nutrient.

ENERGY FROM CARBOHYDRATES, FATS AND PROTEINS

Glucose is not the only molecule to provide energy to living things. A balanced diet is made up of a variety of foods containing **nutrients** such as **carbohydrates** (glucose is an example), **proteins** and **fats**. Nutrients are substances used by an organism to survive, grow and reproduce. Food supplies the energy required for the millions of chemical reactions that occur in your body. Energy is needed for physical activity, for warmth and for functions such as breathing. Energy is also required to build the large molecules in our systems and this energy can be released as the molecules are digested, or **metabolised**, back to smaller units.

Carbohydrates

Carbohydrates are made from the elements carbon, hydrogen and oxygen, and usually have the general formula, $C_x(H_2O)_y$. Many important carbohydrates are polymers of glucose, such as starch, which is used as an energy storage molecule in plants. Figure 2.3.5 shows the repeating glucose units in a polymer of starch. During digestion, **enzymes** in our saliva and small intestine break the starch molecules back into glucose. Enzymes are organic catalysts that alter the rate of biochemical reactions. The glucose is transported in the blood to body cells where respiration can occur. Energy is required to form the many bonds in these large carbohydrates and that energy is released during digestion.

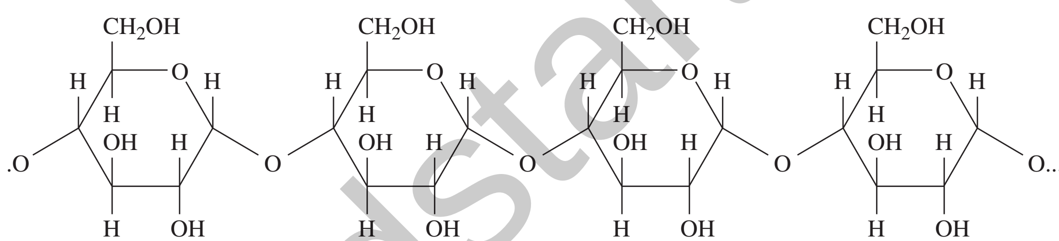


FIGURE 2.3.5 Starch is a natural polymer formed from the polymerisation of glucose monomers. Note: Due to the complexity of the structure the carbon atoms in the rings have been omitted for clarity.

Fats and oils

Fats and oils are examples of triglycerides, large non-polar molecules with three long hydrocarbon chains attached to a glycerol molecule. The general structure of a triglyceride is shown in Figure 2.3.6. Fats play an important role in providing and storing energy in the body. Digestion breaks down fats and components of this breakdown can be oxidised in body cells to carbon dioxide and water, releasing large quantities of energy.

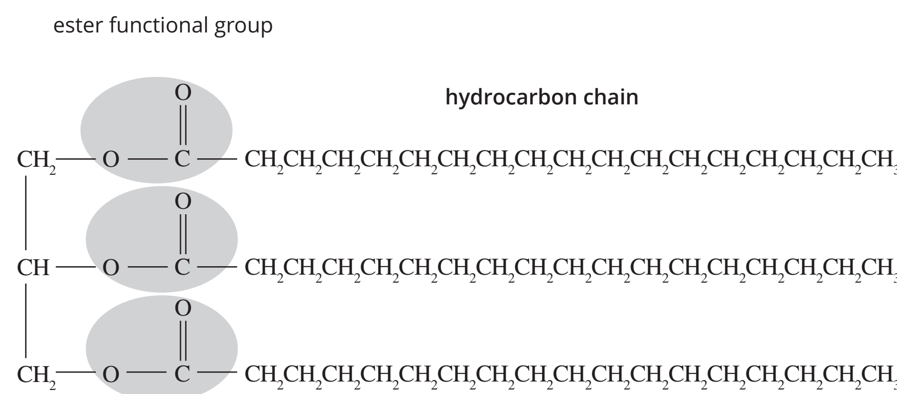


FIGURE 2.3.6 General structure of a triglyceride. Note the three long hydrocarbon chains and the three ester functional groups.

Proteins

A segment of a typical protein molecule is shown in Figure 2.3.7. Proteins are rarely used by the body as an energy source as they have so many other important roles in the body. If, however, intensive exercise depletes the body's stores of glycogen and fat, protein can be used as an alternative. When this occurs, it is important to replace the protein quickly to ensure the functioning of other processes.

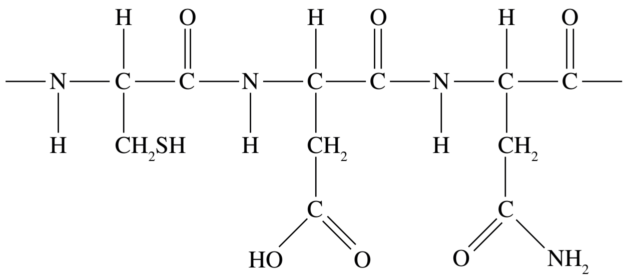


FIGURE 2.3.7 A section of a protein chain

Energy content of carbohydrates, fats and proteins

Each of these three major nutrients provides a different quantity of energy per gram.

The **energy content** of foods—the amount of energy a food or fuel can supply—is measured in kJ g^{-1}, kJ/100 g or even kJ mol^{-1} if the food is a pure substance such as glucose. For most foods, the energy released on combustion is similar to the energy released when the food is oxidised during respiration.

For convenience, each of the major food nutrients—carbohydrates, fats and proteins—are considered to have a particular heat of combustion, although there is a range of values for different members of these food groups. For example, carbohydrates are considered to have a heat of combustion of 16 kJ g^{-1}, whereas the heat of combustion of glucose is 15.7 kJ g^{-1} and that of polysaccharides is 17.6 kJ g^{-1}.

Table 2.3.1 compares the heats of combustion (energy content) and energy available to the body for each of the major food groups. The energy available to the body from a nutrient or food is called its **energy value**. The energy value of different foods will be discussed further in Chapter 3.

TABLE 2.3.1 Comparison of the heat of combustion and energy available to the human body of the three main nutrients

Nutrient	Energy content (heat of combustion kJ g^{-1})	Energy value (energy available for the body kJ g^{-1})
carbohydrates	16	16
fats and oils	39	37
proteins	24	17

Note that fats and oils have a significantly higher energy value than carbohydrates and proteins. This is essentially due to the degree to which these molecules can be oxidised. Carbohydrates tend to contain more oxygen atoms than fats and oils do. At a simple level, the carbon atoms in carbohydrate molecules have a higher 'degree of oxidation'. Therefore, fats and oils have greater potential for oxidation and release more energy on combustion.

The energy released when food is burned is often greater than the energy that is available for the human body to use after the food has been digested. For example, dietary fibre is mainly the carbohydrate cellulose. Humans cannot digest most fibre, so the energy it contains is not available to humans.

2.3 Review

SUMMARY

- Green plants use the energy from the Sun for photosynthesis, the conversion of carbon dioxide and water to glucose and oxygen. The equation for photosynthesis is:

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6O_2(g) \quad \Delta H = +2803 \text{ kJ}$$

- Plants and animals use cellular respiration to oxidise glucose to obtain energy. The equation is the reverse of photosynthesis:

$$C_6H_{12}O_6(aq) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) \quad \Delta H = -2803 \text{ kJ}$$

- The metabolism in the body of carbohydrates, fats and proteins is a source of energy for animals.
- Fats produce the most energy per gram of the major food groups followed by proteins, then carbohydrates.
- The human body will often obtain less energy from a food item than the theoretical quantity based on direct combustion of the food.

KEY QUESTIONS

Knowledge and understanding

1 Name three conditions (including chemicals) that are essential for photosynthesis to occur.

2 It is stated in this section that glucose is a key molecule for the energy processes in living things.
- **a** Explain why glucose is considered a starting point for energy systems.
- **b** Explain the role of glucose in energy storage for plants.
- **c** Explain the role of glucose in energy processes for humans.

3 Complete the following sentences by selecting the correct term for each of the alternatives in bold:
In **cellular/anaerobic** respiration, glucose is used by cells to obtain energy. Aerobic respiration is an **endothermic/exothermic** process in which the glucose is **oxidised/reduced** by **carbon dioxide/oxygen**. A relatively large quantity of energy is **absorbed/released** during aerobic respiration and can be used by the cells of the body.

Analysis

4 State whether each of the following is endothermic or exothermic.
- **a** respiration
- **b** digestion of fish oil
- **c** formation of cellulose from glucose in plants
- **d** photosynthesis
- **e** digestion of starch.

5 Explain how the molecular formulas of fats and carbohydrates indicate which will release the most energy.

6 Cellular respiration is an example of an oxidation reaction. What definition of oxidation best describes this reaction?

2.4 Bioethanol

Ethanol is used as an energy source in combustion engines, fuel cells and electricity generators. Ethanol can be produced from ethene obtained from crude oil but this adds to the problems already mentioned relating to fossil fuels. If, however, the ethanol is produced from **biomass** the environmental concerns are not as significant. Given Australia's strong farming and forestry industries, there is considerable interest in producing bioethanol from the biomass wastes. In this section, you will look at how bioethanol is produced and learn about the potential sources of biomass.

FERMENTATION

Bioethanol is produced from glucose and other sugars in a **fermentation** process. Various enzymes and microorganisms catalyse or facilitate the reactions involved. The process is carried out at 35°C because at higher temperatures, the microorganisms and enzymes would be destroyed. The main reaction is:

$$C_6H_{12}O_6(aq) \longrightarrow 2CH_3CH_2OH(aq) + 2CO_2(g)$$

Fermentation is a natural process in which an organism converts a carbohydrate such as starch or sugar into an alcohol.

Glucose is present in plants as glucose itself and also as a component of larger carbohydrates. The bioethanol industry therefore needs abundant carbohydrate sources that can be broken down to glucose. In the future, the three main bioethanol feedstocks in Australia are likely to be:

- sugar cane (high in sucrose)
- wheat (high in starch)
- forest waste (high in cellulose).

Figure 2.4.1 is an outline of the chemical changes occurring in the bioethanol manufacturing process. The carbohydrates are pulped with water, a process that involves blending the biomass in water to break up the cell or plant structures. Various enzymes are then added to the mixture to break the carbohydrate molecules down to form glucose. Enzymes catalyse the fermentation of glucose to produce an ethanol solution.

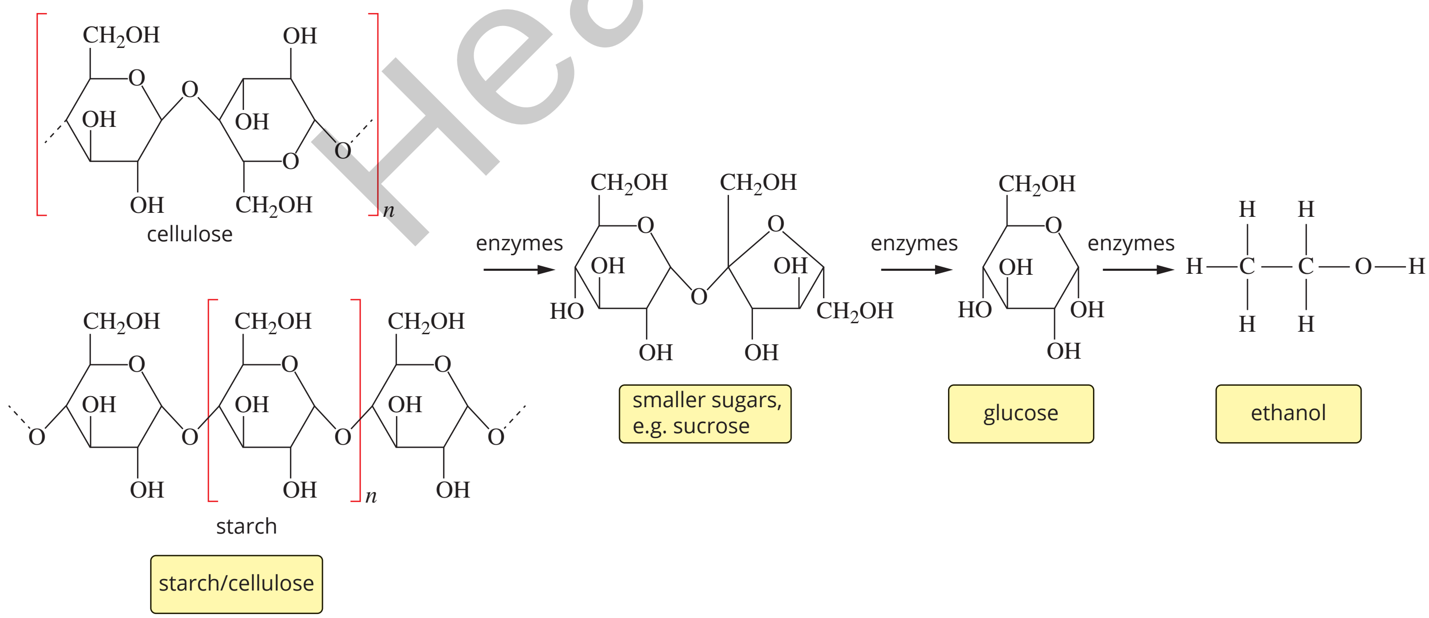


FIGURE 2.4.1 Enzymes are used to break large carbohydrates down to glucose. The complexity of this process depends upon the raw material used.

Figure 2.4.2 provides a more detailed flow chart of the fermentation process. The stronger the bonding in the carbohydrate feedstock, the greater the pre-treatment required to ensure the enzymes are effective. Cellulose, in particular, is abundant as forest waste but difficult to process as the hydrogen bonds holding the cellulose molecules together are relatively strong. In contrast, sugar cane contains smaller and highly soluble sucrose molecules that require no pre-treatment.

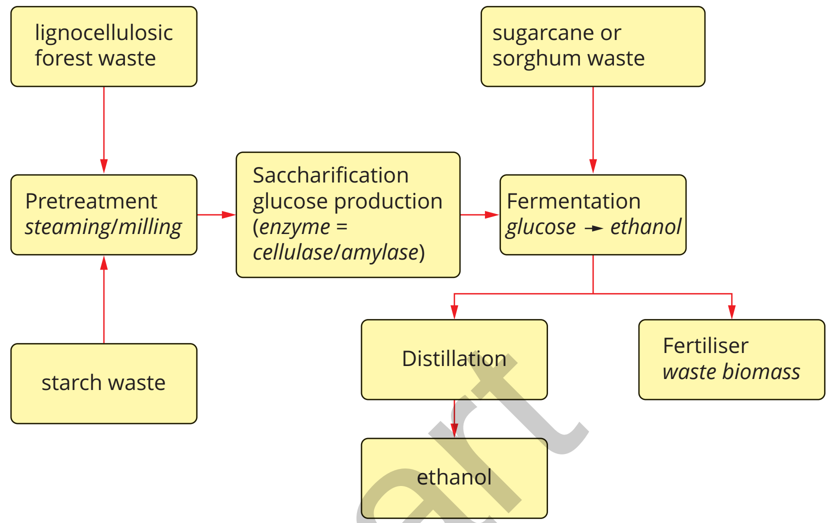


FIGURE 2.4.2 Stages of bioethanol production. The feedstock used varies with available carbohydrate resources.

DISTILLATION

Distillation is the process of separating the components or substances from a liquid mixture by using selective boiling and condensation.

Fermentation produces a solution that is about 10 (%v/v) ethanol. The ethanol needs to be separated from the water for ethanol to be useful as a fuel. **Distillation**, a process that utilises the different boiling points of the liquids, is used to separate the two liquids. The solution is heated to boiling, then fed into tall distillation columns such as the ones shown in Figure 2.4.3. The temperature of the column is carefully controlled so that water (boiling point is 100°C) falls to the bottom of the column while the ethanol gas (boiling point is 79°C) is collected from the top of the column (see Figure 2.4.4 on the following page). The ethanol, at this point, still contains traces of water that are then removed using micro-filtration and dehydrating agents. You will learn more about distillation in Section 13.1.

A small percentage of methanol is usually added to ethanol sold in Australia to make it unfit for human consumption, hence its common name 'methylated spirits'.

The distillation process is relatively straightforward but it requires a significant quantity of energy to boil the ethanol solution. The energy required means bioethanol production is not a carbon-neutral process.

FIGURE 2.4.3 Tall distillation columns such as these ones at Manildra in NSW are common to all bioethanol plants.

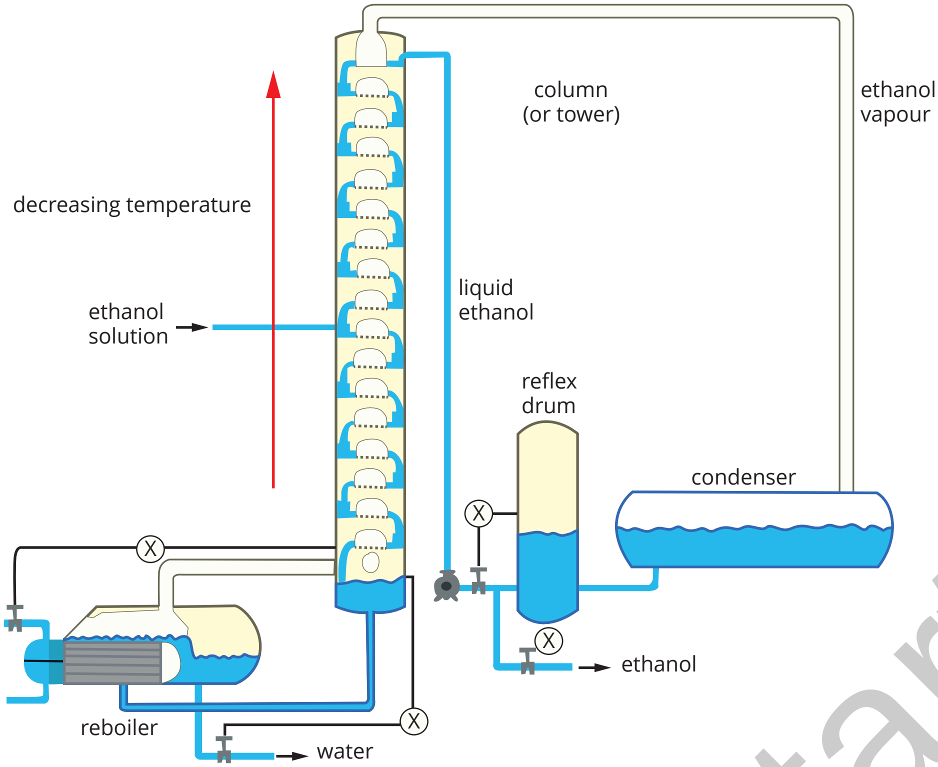


FIGURE 2.4.4 Ethanol is collected from the top of the distillation column and water from the bottom.

THE AUSTRALIAN BIOETHANOL INDUSTRY

Australia has three commercial bioethanol manufacturing plants. Table 2.4.1 summarises the feedstock and capacity of each operation. If more biomass was readily available, this volume could easily be increased as the resultant bioethanol could be blended with petrol.

TABLE 2.4.1 Australia's commercial bioethanol plants

Plant	Location	Feedstock	Annual production (ML)
Manildra	Nowra NSW	wheat waste	300
Wilmar	Sarina QLD	molasses from sugar cane	60
United Petroleum	Dalby QLD	sorghum syrup	46

All three plants are located in a particular region where the feedstock crop is grown so the waste materials can be easily collected for fermentation. Figure 2.4.5a shows the United Petroleum plant in Dalby, Queensland, and Figure 2.4.5b shows its raw material, a sorghum crop ready for harvest. Sorghum is grown to provide feed for cattle, pigs and poultry. Its high starch content makes it ideal for bioethanol production.

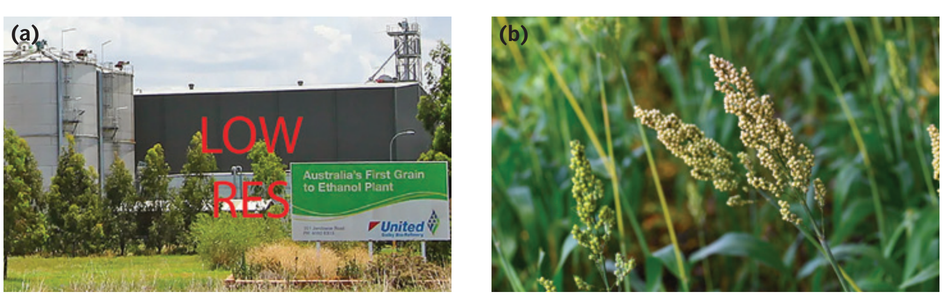


FIGURE 2.4.5 Waste materials from sorghum crops are used in United Petroleum's biodiesel plant at Dalby, Queensland.

CHEMFILE

Solving the ethanol crisis during COVID-19

As COVID-19 reached Australia in 2020, many new sources of ethanol emerged.

The arrival of COVID-19 in 2020 was accompanied by universal advice for people to wash and sanitise their hands frequently. The major component of hand sanitiser is alcohol, either ethanol or propan-2-ol. This advice quickly led to a world shortage of ethanol. The solution to this problem came from an unlikely source, Australia's gin-making companies. The ethanol in gin is the same ethanol as used in hand sanitiser, but hand sanitiser does not require aging or oak storage! As the text in the figure above shows, Australian distilleries quickly adapted production to launch a whole new range of sanitising products. In a concerning twist to the story, the Apollo Bay Distillery in Victoria had to issue a recall of one of their gins in 2020 when the bottles were found to incorrectly contain hand sanitiser.

BIOETHANOL POTENTIAL

FIGURE 2.4.6 Bioethanol can be produced from corn, but is the corn more valuable as a food?

While sugar cane is an obvious source of sugar to use for fermentation, it is also needed for table sugar production, so there are limits to the amounts of bioethanol that can be produced in this way. The same dilemma extends to other foods such as corn. Brazil is one of the world's leading producers of corn, but corn is also an important food staple. Figure 2.4.6 suggests that a balance needs to be maintained between ensuring that basic nutrition needs are met and that vehicles are powered in an environmentally responsible manner.

Chemists are trialling less valuable sources of sugar and starch for bioethanol production. Forest waste is an obvious target. Australia has a large timber industry and there is little use for the bark and trimmings produced. The cellulose in forest waste is a polymer of glucose but it takes harsh pre-treatment with steam and specialised enzymes to break the cellulose into glucose.

Comparison of E10 and petrol

Bioethanol is used extensively in Australia, often in a blend with petrol. Australian government regulations limit the proportion of ethanol in petrol to 10%. This petrol blend is labelled E10 and sold at most Australian service stations. Motoring bodies provide advice on the suitability of E10 fuel for each model of car. Regulations in Queensland are different to other states as they have attempted to support local sugar cane growers by mandating that the volume of ethanol sold in fuel be at least 4% of the total petrol volume sold. The presence of ethanol reduces the emissions of particulates and gases such as oxides of nitrogen, but high levels of ethanol can damage engines, especially in older vehicles. An overall increase in the volume of bioethanol blended into petrol should produce less overall emissions and less demand on scarce fossil fuel reserves.

The equation for the combustion of ethanol is:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H = -1360 \text{ kJ}$$

The combustion of 1 mole of ethanol releases 1360 kJ of energy, equivalent to 29.6 kJ g^{-1}. The energy content of ethanol is about 62% that of petrol, so a larger mass (and volume) of ethanol is required to provide the same quantity of energy. At a simple level, the lower energy content of ethanol can be regarded as the result of the carbon atoms in an ethanol molecule being partly oxidised ('partly burnt'). Some oxygen is already present in the ethanol molecules. E10 fuel and petrol are compared in Table 2.4.2

TABLE 2.4.2 Comparison of E10 and petrol

E10	Petrol
lower energy density, 46 kJ g^{-1} cheaper cleaner combustion can be a renewable fuel absorbs CO_2 during formation to negate the impact of CO_2 emissions during combustion—lower net CO_2 emissions generally safer production	higher energy density, 48 kJ g^{-1} more widely distributed less CO_2 produced per km when driving

CHEMFILE

Ethtec: Ethanol plants of the future

Ethtec (Ethanol Technologies) has established a bioethanol pilot plant near Mussellbrook in the Hunter Valley of New South Wales. This pilot is a 'next generation' plant because it is not focused on taking one source of waste and converting it to one product. Instead it is looking at taking any available biomass in the district and producing a range of useful products.

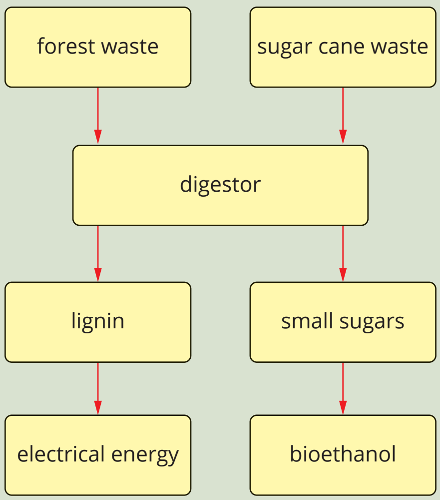


FIGURE 2.4.7 A flow chart showing how multiple sources of biomass can be used to produce multiple useful products

Mussellbrook was chosen as both sugar cane and timber are grown in the region. The waste from both industries is collected for the pilot plant. The forest waste is referred to as lignocellulosic waste as it contains high proportions of both cellulose and lignin. Lignin is a natural polymer present in the cells of all plants. The forest waste is pulped and heated with acid to break down (hydrolyse) cellulose to smaller sugars and to remove the lignin. The process being trialled is outlined in Figure 2.4.7 as a flow chart and Figure 2.4.8 shows the equipment in the plant itself.

FIGURE 2.4.8 Ethtec trial plant with biomass fermentation tanks on the left of the photo

2.4 Review

OA ✓✓

SUMMARY

- Bioethanol can be produced by fermentation of carbohydrates and sugars.
  The fermentation equation is
  $C_6H_{12}O_6(aq) \longrightarrow 2CH_3CH_2OH(aq) + 2CO_2(g)$
- Bioethanol solutions are distilled to separate the ethanol from the water. Ethanol has a lower boiling point than water.
- Australia has commercial plants producing bioethanol. The carbohydrate sources are biomass from sugarcane, sorghum and wheat.
- Bioethanol is sold as E10, which is composed of petrol blended with up to 10% ethanol.
- The energy density of ethanol is lower than that of petrol.

KEY QUESTIONS

Knowledge and understanding

1 **a** Draw a molecule of ethanol.
b Explain why ethanol is soluble in water.
c Write a balanced equation for the complete combustion of ethanol.

2 Classify each of the following as an advantage or a disadvantage of the use of bioethanol compared to petrol as an energy source.
a Can absorb small amounts of water
b Lower energy content ($kJ\ g^{-1}$)
c Can be produced from potato peel waste at a commercial chip manufacturing plant.
d Renewable resource
e Greater amount of CO_2 emitted to travel a set distance
f Lubricates engine moving parts

3 State two reasons why the production of bioethanol from the molasses in sugar cane is a simpler process than from forest waste.

4 Fermentation is typically conducted at temperatures around 35°C. It is a relatively slow reaction. Explain why high temperatures are not used to increase the reaction rate.

Analysis

5 Bioenergy supporters would like to see the volume of E10, in which the ethanol is bioethanol, used in Australia increase significantly. Describe the impact on CO_2 levels of an increase in E10 use.

6 Explain why bioethanol and biodiesel are more likely to be transported from where they are made than biogas.

7 Explain why distillation is required in the manufacture of bioethanol but not biodiesel or biogas.

2.5 Energy from the combustion of fuels

Bushfires are an example of uncontrolled combustion. They can destroy homes and lives, devastating huge areas of bush and damaging the habitat of many animals. As the impact of climate change leads to increased weather extremes in Australia, the threat posed by bushfires has also increased, and fire-control experts are turning to Indigenous Australian experts for assistance with fire prevention.

Indigenous rangers are critical for managing controlled burns in the Kimberley region in northern Australia (Figure 2.5.1a). Highly skilled, they use traditional knowledge and techniques, together with modern science and technology, to fight fire with fire to reduce the likelihood of wildfires. The Kimberley Land Council's Indigenous Fire Management Program is extremely important to the biodiversity of this remote region.

Similarly, in 2021, Indigenous Australian leaders and University of Melbourne researchers collaborated on a submission to the Inquiry into the 2019–20 Victorian fire season recommending a return to cultural burning practices to limit the likelihood of further bushfires (Figure 2.5.1b).

In recognition of the success of programs such as the one in the Kimberley, the Federal Government announced a $200 million collaboration on fire prevention between Indigenous and conventional land managers in March 2021. The grants will deliver a range of workshops, cultural burn demonstrations and community engagement and education programs.

Fire results from the combustion of substances. Combustion reactions need three things:

- fuel to burn
- oxygen for the fuel to burn in
- energy to get the process started.

Fire can be understood and controlled by applying your knowledge of chemistry. In this section, you will learn about combustion reactions and their various representations in more detail.

FIGURE 2.5.1 (a) Indigenous ranger overseeing a controlled burn. (b) In the summer of 2019–2020, large areas of Eastern Victoria were devastated by bushfires.

Combustion reactions are exothermic reactions in which the reactant combines with oxygen to produce oxides. This type of reaction is often referred to as an **oxidation** reaction. The combustion of a hydrocarbon produces carbon dioxide and water, provided there is enough oxygen present.

In redox reactions that involve oxygen as a reactant, oxidation can be defined as the addition of oxygen to form oxides, such as in a combustion reaction.

COMPLETE AND INCOMPLETE COMBUSTION

Combustion reactions can be described as complete or incomplete. The difference between the two is due to the amount of oxygen available to react with the fuel.

Complete combustion occurs when oxygen is plentiful. The only products are carbon dioxide and water.

An example is the complete combustion of methane:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

When oxygen is not plentiful, incomplete combustion of fuels occurs. The products of incomplete combustion are carbon monoxide and/or carbon and water.

CHEMFILE

Carbon monoxide poisoning

Carbon monoxide is a highly poisonous gas. It combines readily with haemoglobin, the oxygen carrier in blood. When attached to carbon monoxide, haemoglobin cannot transport oxygen around the body, which leads to oxygen starvation of tissues.

Even at concentrations as low as 10 parts per million (ppm), carbon monoxide can cause drowsiness, dizziness and headaches. At about 200 ppm, carbon monoxide can lead to death. The average carbon monoxide concentration in large cities, mostly due to incomplete combustion of fuels in cars, is now 7 ppm, but it can be as high as 120 ppm at busy intersections in heavy traffic.

Car exhaust gases can contain high levels of carbon monoxide as a result of incomplete combustion of fuels.

FIGURE 2.5.2 The yellow flame of a Bunsen burner is due to incomplete combustion and produces carbon as a product. The blue flame is a hotter flame that occurs when the air hole is open and more oxygen is allowed to react, resulting in compete combustion.

When the oxygen supply is limited, **incomplete combustion** occurs. As less oxygen is available, not all of the carbon can be converted into carbon dioxide. Carbon monoxide and/or carbon are produced instead. The hydrocarbon burns with a yellow, smoky or sooty flame due to the presence of glowing carbon particles. Figure 2.5.2 shows the appearance of the different flames of a Bunsen burner due to incomplete and complete combustion.

The equation for the incomplete combustion of methane to form carbon monoxide is:

$$2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(l)$$

Writing equations for complete combustion of fuels

It is important to write chemical equations correctly because they tell you a lot about chemical reactions. Writing equations for the complete combustion reactions of fuels containing carbon and hydrogen is relatively straightforward, because the products are always carbon dioxide and water.

Perhaps the most important of all combustion reactions involving fuels are those that occur when petrol is burnt. Petrol is a mixture of hydrocarbons, including octane.

The combustion reactions of octane (C_8H_{18}) and the other hydrocarbons in petrol power the internal combustion engines in most of Australia's motor vehicles.

Worked example 2.5.1

WRITING EQUATIONS FOR COMPLETE COMBUSTION OF HYDROCARBON FUELS

Write the equation, including state symbols, for the complete combustion of butane (C_4H_{10}).

Thinking	Working
Add oxygen as a reactant and carbon dioxide and water as the products.	$C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$
Balance carbon and hydrogen atoms, based on the formula of the hydrocarbon.	$C_4H_{10} + O_2 \rightarrow 4CO_2 + 5H_2O$
Find the total number of oxygen atoms on the product side.	Total O $= (4 \times 2) + 5$ $= 13$
If this is an odd number, multiply all of the coefficients in the equation by two, except for the coefficient of oxygen.	$2C_4H_{10} + O_2 \rightarrow 8CO_2 + 10H_2O$
Balance oxygen by adding the appropriate coefficient to the reactant side of the equation.	$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$
Add state symbols.	$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$

Worked example: Try yourself 2.5.1

WRITING EQUATIONS FOR COMPLETE COMBUSTION OF HYDROCARBON FUELS

Write the equation, including state symbols, for the complete combustion of hexane (C_6H_{14}).

A similar series of steps can also be used to write the combustion equations for other carbon-based fuels that contain oxygen, for example, alcohols.

Worked example 2.5.2

WRITING EQUATIONS FOR COMBUSTION REACTIONS OF ALCOHOLS

Write the equation, including state symbols, for the complete combustion of liquid ethanol (C_2H_5OH).

Thinking	Working
Add oxygen as a reactant and carbon dioxide and water as the products.	$C_2H_5OH + O_2 \longrightarrow CO_2 + H_2O$
Balance carbon and hydrogen atoms, based on the formula of the alcohol.	$C_2H_5OH + O_2 \longrightarrow 2CO_2 + 3H_2O$
Find the total number of oxygen atoms on the product side. Then subtract the one oxygen atom in the alcohol molecule from the total number of oxygen atoms on the product side.	Total O on product side $= (2 \times 2) + 3$ $= 7$ Total O on product side – 1 in alcohol $= 7 - 1 = 6$
If this is an odd number, multiply all the coefficients in the equation by two, except for the coefficient of oxygen.	$C_2H_5OH + O_2 \longrightarrow 2CO_2 + 3H_2O$
Balance oxygen by adding the appropriate coefficient to the reactant side of the equation.	$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$
Add state symbols.	$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

Worked example: Try yourself 2.5.2

WRITING EQUATIONS FOR COMBUSTION REACTIONS OF ALCOHOLS

Write the equation, including state symbols, for the complete combustion of liquid methanol (CH_3OH).

Writing equations for incomplete combustion of fuels

When the supply of oxygen is insufficient, incomplete combustion of fuels occurs. Equations can also be written to represent this. In general, for the incomplete combustion of hydrocarbons, as well as carbon-based fuels that contain oxygen, the products are carbon monoxide and/or carbon and water.

Worked example 2.5.3

WRITING EQUATIONS FOR INCOMPLETE COMBUSTION OF FUELS

Write an equation, including state symbols, for the incomplete combustion of ethane gas (C_2H_6). The only carbon product is carbon monoxide.

Thinking	Working
Add oxygen as a reactant and carbon monoxide and water as the products.	$C_2H_6 + O_2 \rightarrow CO + H_2O$
Balance the carbon and hydrogen atoms, based on the formula of the hydrocarbon.	$C_2H_6 + O_2 \rightarrow 2CO + 3H_2O$
Balance oxygen by adding the appropriate coefficient to the reactant side of the equation.	$C_2H_6 + \frac{5}{2}O_2 \rightarrow 2CO + 3H_2O$
If oxygen gas has a coefficient that is half of a whole number, multiply all of the coefficients in the equation by two.	$2C_2H_6 + 5O_2 \rightarrow 4CO + 6H_2O$
Add state symbols.	$2C_2H_6(g) + 5O_2(g) \rightarrow 4CO(g) + 6H_2O(l)$

Worked example: Try yourself 2.5.3

WRITING EQUATIONS FOR INCOMPLETE COMBUSTION OF FUELS

Write an equation, including state symbols, for the incomplete combustion of liquid methanol (CH_3OH). The only carbon product is carbon monoxide.

The heat of combustion is usually measured at conditions of 298 K and 100 kPa. This means the water produced should be shown in the liquid state.

Only fuels that exist as pure substances can have their heat of combustion measured in kJ mol^{-1}.

HEAT OF COMBUSTION

The **heat of combustion** of a fuel can be defined as the heat energy released when a specified amount (e.g. 1 g, 1 L, 1 mol) of a substance burns completely in oxygen and is therefore a positive value. It is usually measured under the standard conditions of 298 K and 100 kPa, which means that the water produced should be shown in the liquid state. In comparison, the **enthalpy of combustion**, ΔH_c, which is found in a thermochemical equation, would have a negative value, indicating the exothermic nature of the combustion reaction.

Many fuels, including wood, coal and kerosene, are mixtures of chemicals and do not have a specific chemical formula or molar mass. This means their heat of combustion cannot be expressed in kJ mol^{-1}. Therefore, the heat of combustion of these fuels are measured only as kJ g^{-1} or kJ L^{-1}.

The heats of combustion for some common elements and compounds present in fuels are listed in Table 2.5.1. Notice that the heats of combustion are written as positive values, showing the quantity of energy released.

TABLE 2.5.1 Heats of combustion for some common elements and compounds

Substance	Heat of combustion (kJ mol^{-1})
methane	890
ethane	1560
propane	2220
butane	2880
octane	5460
methanol	725
ethanol	1360
hydrogen	282
carbon (graphite)	394

Another term associated with the energy content of fuels is molar enthalpy. **Molar enthalpy** is the enthalpy of a substance given per mole and is essentially the same as enthalpy of combustion for a fuel.

As Worked example 2.5.4 shows, you can use heat of combustion data to calculate the energy released on combustion of a specified mass of one of the fuels. The energy released when n mol of a fuel burns is given by the equation:

$$\text{energy} = n \times \Delta H_c$$

Worked example 2.5.4

CALCULATING ENERGY RELEASED BY A SPECIFIED MASS OF A PURE FUEL

Calculate the quantity of energy released when 3.60 kg of pentane (C_5H_{12}) is burnt in an unlimited supply of oxygen. The molar heat of combustion of pentane is 3510 kJ mol^{-1}.

Thinking	Working
Calculate the number of moles of the compound using: $n = \frac{m\text{(in grams)}}{M}$	$n(C_5H_{12}) = \frac{m}{M} = \frac{3.60 \times 10^3}{72} = 50.0$ mol
Multiply the number of moles by the heat of combustion per mole.	Energy $= n \times \Delta H_c = 50.0 \times 3510 = 1.76 \times 10^5$ kJ

Worked example: Try yourself 2.5.4

CALCULATING ENERGY RELEASED BY A SPECIFIED MASS OF A PURE FUEL

Calculate the quantity of energy released when 5.40 kg of propanol (C_3H_8O) is burnt in an unlimited supply of oxygen. The molar heat of combustion of propanol is 2020 kJ mol^{-1}.

Energy content

The energy content of a fuel is often expressed in units of kilojoules per gram.

For a pure substance, the heat of combustion per gram can be calculated by simply dividing the heat of combustion per mole (kJ mol^{-1}) by the molar mass of the substance.

For example, for ethanol:

Heat of combustion per mole = 1360 kJ mol^{-1}

Molar mass = 46.0 g mol^{-1}

$$\text{Heat of combustion per gram} = \frac{1360}{46.0} = 29.6 \text{ kJ g}^{-1}$$

For fuels that are mixtures, approximate values for the heat of combustion per gram are shown in Table 2.5.2.

TABLE 2.5.2 Approximate heat of combustion values for some fuel mixtures

Substance	State	Heat of combustion (kJ g^{-1}) (approx.)
kerosene	liquid	18
wood	solid	21
diesel	liquid	25
black coal	solid	25
natural gas	gas	30

Energy content per gram can be a useful comparison when determining the suitability of transport fuels.

Petrol has a higher energy per gram than bioethanol. This means more E10 fuel is required to produce the same amount of energy as petrol.

THERMOCHEMICAL EQUATIONS

As you learnt in Section 2.1, thermochemical equations can be used to compare energy changes. Thermochemical equations include a sign and numerical value for the energy change that occurs in the reaction. The thermochemical equation for the complete combustion of propane is:

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H = -2220 \text{ kJ}$$

The above equation tells us:

- the complete combustion of 1 mole of propane gas and 5 moles of oxygen gas to carbon dioxide and water releases 2220 kJ of energy
- the molar enthalpy of combustion for propane is –2220 kJ mol^{-1}
- the reaction is exothermic
- propane is likely to be a useful fuel as the magnitude of the energy change is relatively high
- the use of propane as a fuel will be associated with greenhouse gas emission issues since CO_2 is a product.

Thermochemical equations and mole ratios

The ΔH value in a thermochemical equation corresponds to the mole amounts specified by the equation. If the coefficients in the equation are changed, the ΔH value will also change.

For example, the thermochemical equation for the combustion of methanol can be written as:

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -726 \text{ kJ}$$

This means that 726 kJ of energy is released when 1 mole of methanol reacts with 1.5 moles of oxygen gas, to produce 1 mole of carbon dioxide and 2 moles of water.

If twice as much methanol were to react, then twice as much energy would be released. So, if the coefficients of the equation are doubled, the ΔH value is also doubled:

$$2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l) \qquad \Delta H = -1452 \text{ kJ}$$

If the mole amounts are tripled, the ΔH value is also tripled:

$$3CH_3OH(l) + 4\frac{1}{2}O_1(g) \longrightarrow 3CO_2(g) + 6H_2O(l) \qquad \Delta H = -2178 \text{ kJ}$$

Effect on ΔH of reversing a chemical reaction

Reversing a chemical equation changes the sign but not the magnitude of ΔH.

For example, methane reacts with oxygen gas to produce carbon dioxide gas and water in an exothermic reaction:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890 \text{ kJ}$$

If this reaction is reversed, the magnitude of ΔH remains the same because the enthalpies of the individual chemicals have not changed, but the sign changes to indicate that energy must be absorbed for this reaction to proceed.

$$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g) \qquad \Delta H = +890 \text{ kJ}$$

Worked example 2.5.5

CALCULATING ΔH FOR ONE EQUATION USING ANOTHER EQUATION

Iron reacts with oxygen according to the equation:

$$3Fe(s) + 2O_2(g) \longrightarrow Fe_3O_4(s) \qquad \Delta H = -1121 \text{ kJ}$$

Calculate ΔH for the reaction represented by the equation:

$$2Fe_3O_4(s) \longrightarrow 6Fe(s) + 4O_2(g)$$

Thinking	Working
The reaction has been reversed in the second equation, so the sign for ΔH is changed to the opposite sign.	ΔH for the second equation is positive.
Identify how the coefficients in the equation have changed.	The coefficient for Fe_3O_4 has changed from 1 to 2, O_2 has changed from 2 to 4 and Fe has changed from 3 to 6. They have all doubled.
Identify how the magnitude of ΔH will have changed for the second equation.	The coefficients in the equations have all doubled, so ΔH will also have doubled.
Calculate the new magnitude of ΔH. (You will write the sign of ΔH in the next step.)	2×1121 $= 2242$
Write ΔH for the second equation, including the sign.	$\Delta H = +2242$ kJ

Worked example: Try yourself 2.5.5

CALCULATING ΔH FOR ONE EQUATION USING ANOTHER EQUATION

Carbon reacts with hydrogen according to the equation:

$$6C(s) + 3H_2(g) \longrightarrow C_6H_6(g) \qquad \Delta H = +49 \text{ kJ}$$

Calculate ΔH for the reaction represented by the equation:

$$3C_6H_6(g) \longrightarrow 18C(s) + 9H_2(g)$$

THE IMPORTANCE OF STATES

Enthalpy changes also occur during physical changes, so thermochemical equations can be written for physical changes. Boiling water is an example of a physical change. It is an endothermic process, because heat must be applied to liquid water to convert it into steam. The thermochemical equation for this reaction is:

$$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta H = +40.7 \text{ kJ}$$

The ΔH value is positive because this is an endothermic reaction.

The thermochemical equation for the combustion of propane was shown above. You can see in the two equations below that the enthalpy value quoted depends upon whether the water produced is shown as a gas or a liquid.

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g) \qquad \Delta H = -2057 \text{ kJ}$$

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H = -2220 \text{ kJ}$$

By convention, heats of combustion are calculated at Standard Laboratory Conditions (298 K and 100 kPa) with combustion products being $CO_2(g)$ and $H_2O(l)$.

CASE STUDY **ANALYSIS**

Explosives—a blast of chemical energy

Humans have been using chemicals to make explosions since 919 BCE. In China, people first mixed saltpetre (potassium nitrate), sulfur and charcoal with explosive results. They quickly realised that there were many uses for this mixture, which later became known as gunpowder. It was put to military use and eventually led to the development of bombs, cannons and guns.

Today, explosives are an essential tool for mining and other engineering works, such as road construction, tunnelling, building and demolition (see Figure 2.5.3).

Explosives transform chemical energy into large quantities of thermal energy very quickly. Although thermal energy is also released when fuels such as petrol and natural gas burn, the rate of combustion in these reactions is limited by the availability of oxygen gas to the fuel. In contrast, the compounds making up an explosive contain sufficient oxygen for a complete (or almost complete) reaction to occur very quickly.

When chemical explosives, such as ammonium nitrate, trinitrotoluene (TNT) and nitroglycerine decompose, they release large quantities of energy and gaseous products very quickly.

This is the thermochemical equation for the decomposition of nitroglycerine:

$$4C_3H_5N_3O_9(l) \longrightarrow 12CO_2(g) + 10H_2O(g) + 6N_2(g) + O_2(g) \quad \Delta H = -1456 \text{ kJ}$$

The equation above highlights a common feature of most explosives—a solid or liquid reactant being converted to gaseous products. The gaseous products form very quickly, requiring a much greater space between the particles and subsequently 'exploding' the fuel and surroundings.

FIGURE 2.5.3 An old bridge is demolished with the help of explosives.

At atmospheric pressure, the products of this reaction would expand to fill a volume more than 10 000 times larger than the volume of the reactants! During a blast, this gas is usually produced within a small hole into which the liquid explosive has been placed, creating huge pressures that shatter the surrounding rock or structure.

Analysis

1 Is this reaction exothermic or endothermic? Justify your answer.

2 What is the ratio of moles of products to moles of reactants? How does this make this reaction suitable for a chemical explosion?

3 How much energy would be produced if 8 moles of nitroglycerine were reacted?

4 Explain why this highly explosive reaction can only be started using some type of trigger.

2.5 Review

SUMMARY

- The products of the complete combustion of hydrocarbons and carbon-based fuels containing oxygen are carbon dioxide and water.
- Incomplete combustion occurs when hydrocarbons and carbon-based fuels containing oxygen undergo combustion in a limited supply of oxygen. The products of incomplete combustion include carbon monoxide and/or carbon and water.
- A number of related terms are used when comparing fuels.

  General terms

  Enthalpy: the chemical energy of a substance

  Enthalpy change: difference in chemical energy of the products compared to the reactants

  Molar enthalpy: the enthalpy of a substance given per mole

  Specific term for combustion reactions

  Heat of combustion (of a fuel): the heat energy released when a specified amount (e.g. 1 g, 1 L, 1 mol) of a substance burns completely in oxygen

  Enthalpy of combustion, ΔH_c: a negative value which has the same numerical value as the heat of combustion
- Heats of combustion indicate the maximum quantity of energy that can be released when a specified amount of fuel undergoes complete combustion. Common units are kJ mol^{-1} and kJ g^{-1}. Because these values are a measure of the quantity of energy released, they have a positive value when tabulated.
- The quantity of energy released by different fuels can be compared using their heats of combustion.
- For a pure fuel with a heat of combustion measured in kJ mol^{-1}, the energy released when *n* mol of the fuel burns can be calculated by the equation:

  $$\text{Energy} = n \times \text{heat of combustion}$$
- Combustion reactions are exothermic reactions that can be represented by balanced thermochemical equations. Combustion reactions have a negative ΔH value.
- Reversing an equation causes the sign of ΔH to change, as the reaction changes from exothermic to endothermic, or vice versa.
- Doubling the coefficients in a chemical reaction causes the ΔH value to also double, as twice as many reactants react to produce or absorb twice as much energy.
- States of matter must be included in thermochemical equations because changes of state involve enthalpy changes.
- Heat of combustion data tables can be used to determine the enthalpy change, ΔH, in a thermochemical equation.

KEY QUESTIONS

Knowledge and understanding

1 Write a balanced chemical equation for the complete combustion of liquid benzene (C_6H_6).

2 Write a balanced equation for the incomplete combustion of ethanol (C_2H_5OH) when carbon monoxide is formed.

3 When pentane, C_5H_{12}, combusts, it reacts with oxygen to form carbon dioxide and water. When one mole of pentane combusts, 3509 kJ of energy is released. Write a balanced thermochemical equation for this reaction.

4 A data book lists the heat of combustion of propan-1-ol as 2021 kJ mol^{-1}. Determine the heat of combustion of propan-1-ol in kJ g^{-1}.

5 Use the information in Table 2.5.1 to calculate the quantity of energy released when the following quantities of fuel undergo complete combustion.

a 250 g of methane

b 9.64 kg of propane

c 403 kg of ethanol

6 Define the term 'heat of combustion'.

continued over page

2.5 Review *continued*

Analysis

7 **a** Which will release the most energy — complete or incomplete combustion of propane?

b Explain your answer to part **a**.

8 The thermochemical equation for photosynthesis can be represented as:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$
$$\Delta H = +2803 \text{ kJ}$$

a Determine whether this reaction is endothermic or exothermic. Give a reason for your answer.

b Consider a new reaction that reversed and halved the above reaction. Calculate the energy change of the new reaction that is written below:

$$\frac{1}{2}C_6H_{12}O_6(aq) + 3O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$$

9 The combustion of octane to form carbon dioxide and liquid water can be written as:

$$C_8H_{18}(g) + 12\frac{1}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$$
$$\Delta H = -5450 \text{ kJ}$$

The combustion of octane to form carbon dioxide and steam can be written as:

$$C_8H_{18}(g) + 12\frac{1}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g)$$

The thermochemical equation for the reaction in which liquid water turns into steam is:

$$H_2O(l) \rightarrow H_2O(g) \ \Delta H = +40.7 \text{ kJ}$$

How would the energy released by the combustion of 1 mole of octane to form steam compare with the energy released by 1 mole of octane to form liquid water?

Chapter review

02

KEY TERMS

activation energy
alkane
anaerobic
biodiesel
bioethanol
biofuel
biogas
biomass
carbohydrate
carbon neutral
catalyst
cellular respiration
cellulose
chemical energy
combustion
complete combustion
distillation
endothermic
energy content
energy profile diagram
energy value
enthalpy
enthalpy change
enthalpy of combustion, ΔH_c
enzyme
exothermic
fats
fermentation
fossil fuel
fractional distillation
fuel
heat content
heat of combustion
homologous series
hydrocarbon
incomplete combustion
joule
metabolised
molar enthalpy
natural gas
non-renewable
nutrients
oxidation
petrodiesel
photosynthesis
protein
renewable fuels
renewables
respiration
sustainable
thermochemical equation
transesterification
triglyceride

REVIEW QUESTIONS

Knowledge and understanding

1 Which of the following fuels is used more commonly for transport than electricity generation?
- **A** coal
- **B** biodiesel
- **C** natural gas
- **D** biogas

2 Which one of the following is a renewable form of energy?
- **A** natural gas
- **B** petrol
- **C** gas generated from animal manure
- **D** electrical energy produced in a coal-fired power station where the emissions are stored underground

3 Select the correct statement about E10 fuel.
- **A** E10 does not produce carbon-containing emissions.
- **B** E10 will be less soluble in water than petrol.
- **C** Reserves of E10 are limitless.
- **D** E10 has a lower energy density than petrol.

4 Which one of the following is correct about the energy profile diagrams of both endothermic and exothermic reactions?
- **A** There is always less energy absorbed than released.
- **B** The enthalpy of the products is always less than the energy of the reactants.
- **C** Some energy is always absorbed to break bonds in the reactants.
- **D** The ΔH value is the difference between the enthalpy of the reactants and the highest energy point reached on the energy profile.

5 Label each of the following as exothermic or endothermic.
- **a** ice melting to water
- **b** candle burning
- **c** reaction that causes the surroundings to drop in temperature
- **d** reaction with a negative value of ΔH

6 Explain why fossil fuels are considered to be non-renewable.

7 Calculate the quantity of energy released from complete combustion of:
- **a** 0.740 mol of ethanol
- **b** 12.0 g of ethanol.

8 The combustion of hydrogen is an exothermic reaction:

- **a** Identify the bonds which need to be broken for a reaction to occur.
- **b** Identify the bonds which are formed in the reaction.
- **c** State which quantity is greater for this reaction—the energy required to break bonds or the energy produced from bonds that are formed?
- **d** Explain whether this reaction will increase or decrease the temperature of the surroundings?

9
- **a** Write a balanced overall equation for the photosynthesis reaction.
- **b** Name the important molecule produced in plants by photosynthesis.
- **c** Write a balanced overall equation for the process of aerobic respiration.

10
- **a** Name two common feedstocks that can be used to produce bioethanol.
- **b** Write a balanced equation for the fermentation process.
- **c** What is the role of a distillation column in the production of bioethanol?

11 Write a thermochemical equation for the complete combustion of ethanol.

12 Refer to Table 2.2.1 on page xxx, which lists the typical composition of biogas.

- **a** Which two gases form the largest percentage of a typical biogas sample?
- **b** Why might there be variations in the percentage of gases making up different samples of biogas?

13 Identify whether each of the following statements related to activation energy is true or false.

- **a** Activation energy is the energy required to break bonds in the reactants.
- **b** The activation energy of the forward reaction equals that of the reverse reaction.
- **c** The magnitude of the activation energy is always greater than the enthalpy change.
- **d** All fuels have very low activation energies.

14 Explain why reversing a chemical reaction reverses the sign of ΔH.

15 The combustion of butane gas in portable stoves can be represented by the thermochemical equation:

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(l) \quad \Delta H = -5772 \text{ kJ}$$

- **a** How does the overall energy of the bonds in the reactants compare with the overall energy of the bonds in the products?
- **b** Draw an energy profile diagram for the reaction, labelling ΔH and activation energy.

16
- **a** Write a balanced chemical equation for the complete combustion of propanol (C_3H_7OH).
- **b** Write a balanced chemical equation for the incomplete combustion of pentane (C_5H_{12}) where carbon monoxide is formed.

Application and analysis

17 A sample of biodiesel has been prepared using palmitic acid ($C_{15}H_{31}COOH$) and methanol. Write a balanced equation for the complete combustion of this biodiesel.

18 The combustion reaction of ethyne gas that occurs during welding can be represented by the thermochemical equation:

$$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l) \quad \Delta H = -2619 \text{ kJ}$$

- **a** Is this reaction endothermic or exothermic?
- **b** What would be the new value of ΔH if the equation was now written as follows?

$$4C_2H_2(g) + 10O_2(g) \longrightarrow 8CO_2(g) + 4H_2O(l)$$

19 According to a data table, the heat of combustion of hydrogen is 286 kJ mol^{-1}. Write a balanced thermochemical equation for the complete combustion of hydrogen.

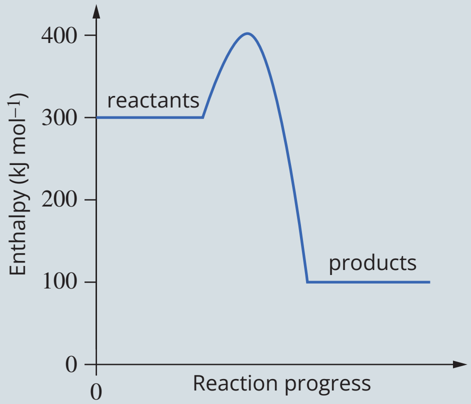
20 Explain why biodiesel made from canola oil is sometimes described as a 'carbon-neutral' fuel. Use a chemical equation to support your answer.

21 Use the terms 'methane', 'oxygen', 'bacteria' and 'carbon dioxide' to explain the formation and composition of biogas.

22 Trials are being conducted to source biogas from cheese. A prototype plant in England uses the whey left over from cheese production. Bacteria act on this cheese waste in anaerobic conditions to produce biogas. Classify the following as advantages or disadvantages of large-scale production of biogas from cheese waste.

- **a** fewer particulate emissions than natural gas
- **b** renewable
- **c** less reliance on fossil fuels
- **d** can only be used on-site
- **e** fewer net CO_2 emissions than natural gas
- **f** raw material needs to be heated in winter
- **g** lower sulfur content than natural gas
- **h** the cheese waste was previously used as a fertiliser.

23 The energy profile diagram below shows the relative enthalpies, on an arbitrary scale, of the reactants and products of a chemical reaction.



a Is the reaction exothermic or endothermic?

b What is the value of the activation energy of the forward and reverse reactions?

c What is the value of ΔH of the reverse reaction?

24 a Calculate the energy available from 1 kg of each of the following fuels, using the information provided in Table 2.5.1 p XX.

i octane, C_8H_{18}

ii butane, C_4H_{10}

iii ethane, C_2H_6

b Use the results of your calculations in part **a** to describe the trend in heats of combustion (in kJ/kg) in the alkane homologous series.

25 In a steelworks, carbon monoxide present in the exhaust gases of the blast furnace can be used as a fuel elsewhere in the plant. It reacts according to the equation:

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -283 \text{ kJ}$$

a Which has the greater total enthalpy: 1 mol of CO(g) and 0.5 mol of O_2(g), or 1 mol of CO_2(g)?

b Write the value of ΔH for the following equations:

i $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

ii $2CO_2(g) \longrightarrow 2CO(g) + O_2(g)$