CHAPTER 12

Resources and the environment

In a chemistry sense, our world is essentially a closed system; that is, there is no net gain or loss of matter in the world. The implications of this are two-fold. First, all physical natural resources are finite (cannot be replaced). Second, the products of the chemical industry will remain in the environment in one form or another.

This presents chemists with a delicate balancing act. On the one hand, society demands and expects a continuous supply of materials and goods, almost all of which involve a chemist in either their design or their production. On the other hand, there is growing concern regarding the long-term sustainability of resources and the health of the environment.

These seemingly contrasting notions are addressed by the philosophy underpinning green chemistry.

Science as a human endeavour

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

12.1 Green chemistry

'Green chemistry' is a term that can be confused with 'environmental chemistry'. Environmental chemistry is the study of chemical processes that occur in a natural environment and how these processes are affected by human activities such as mining or pollution. **Green chemistry** is not a specific discipline of chemistry, but is an overarching philosophy related to **sustainable** and environmentally friendly chemical practices.

Environmental sustainability can be considered as the ability to balance the rates of resource use and pollution so that they can be continued indefinitely without harm to the environment.

The ultimate goal of green chemistry is to design more resource-efficient, environmentally friendly products and processes through technological and engineering solutions.

PRINCIPLES OF GREEN CHEMISTRY

The approach of green chemistry to industrial processes, and to a lesser extent laboratory and research activities, is underpinned by the 12 principles of green chemistry (Table 12.1.1).

TABLE 12.1.1 The 12 principles of green chemistry

Principle	Explanation
1 Prevent waste	Design chemical processes to prevent waste rather than treat waste or clean it up after it is formed.
2 Maximise atom economy	Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
3 Design less hazardous chemical syntheses	Design safer methods that use and generate substances with little or no toxicity to humans and the environment.
4 Design safer chemicals and products	Design chemical products to be fully effective, yet to have little or no toxicity.
5 Use safer solvents and reaction conditions	Avoid using toxic solvents to dissolve reactants or extract products.
6 Increase energy efficiency	Minimise energy requirements. Perform chemical reactions at room temperature and pressure whenever possible.
7 Use renewable raw materials	Use starting materials that are derived from renewable resources, such as plant materials, rather than from finite resources, such as fossil fuels.
8 Avoid chemical derivatives	When a chemical has to be produced from another chemical before it can be used, additional reagents are used and extra waste is generated.
9 Use catalysts, not excess reactants	Minimise waste by using small amounts of catalysts that can carry out a single reaction many times. Using a catalyst is preferable to using excess reactants, which creates waste.
10 Design chemicals and products that are biodegradable	Design chemical products that break down to harmless substances after use so that they do not accumulate in the environment.
11 Analyse in real time to prevent pollution	Include continuous monitoring and control during the process to minimise or eliminate the formation of by-products.
12 Minimise the potential for accidents	Design chemicals and their forms (solid, liquid or gas) to minimise the potential for chemical accidents, including explosions, fires and releases to the environment.

SUSTAINABLE CHEMISTRY

One of the challenges facing politicians and lawmakers is to balance the need for economic growth and jobs with the desire to preserve and protect the natural environment. These are often seen as mutually exclusive, where you can have jobs and growth or a pristine natural environment, but not both.

However, the principles of green chemistry do not conflict with a productive and economically viable chemical industry. Through approaches such as developing alternative chemical syntheses, selecting safer **renewable** and locally sourced reagents, minimising waste and undertaking remediation (environmental clean-up), chemical industries can become sustainable, both environmentally and economically.

A renewable resource is a resource that is replenished naturally at a rate which compensates for its depletion through use.

Remediation is the act of remedying something.

Green syntheses

Industrial chemists design efficient methods for converting readily available starting materials into desired products. This process is known as the **synthesis** of a compound. The chemicals generated by industry could be compounds that have been designed to have exactly the right properties for their intended use, or compounds found in nature but not in large enough quantities required by society.

CHEMISTRY IN ACTION

Insulin: an example of chemical synthesis

In Australia, an estimated one million people have been diagnosed with diabetes. Many of these people require regular injections of insulin. Insulin is a hormone that plays an important role in regulating glucose levels in the blood. Insulin is naturally produced in the pancreas.

FIGURE 12.1.1 These pig pancreases are being examined upon delivery from the abattoir before being ground up for the rest of the extraction process.

When the study of insulin and its role in regulating blood sugar levels began in the early 1920s, the only source of insulin was living organisms, such as pigs and cattle (Figure 12.1.1). Insulin was extracted, purified and injected into mainly children, who were dying from diabetic ketoacidosis, in order to save their lives.

It wasn't until the early 1950s when the amino acid structure of insulin (Figure 12.1.2) was characterised by British biochemist Frederick Sanger that a synthesis was possible. Sanger was awarded the Nobel Prize in Chemistry in 1958 for his work.

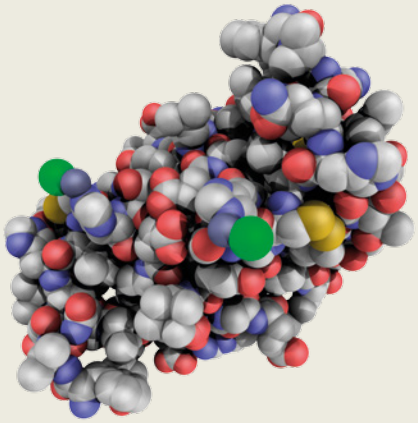


FIGURE 12.1.2 A computer-generated model of an insulin molecule. The chemical structure of insulin took almost 30 years to determine.

FIGURE 12.1.3 Nurofen is a well-known brand of ibuprofen pain killer.

In the past, chemists mainly concerned themselves with the yield and purity of the final products. They also considered time and cost as important factors. With an increasing awareness and concern for the environmental impact of human activities, chemists are trying to develop 'greener' synthesis pathways that minimise unwanted side-products, reduce waste and are energy efficient, while still being industrially feasible and economically viable.

Ibuprofen (Figure 12.1.3) is a common analgesic (pain reliever) that was first developed in the 1950s. Its 'brown' synthesis pathway (Figure 12.1.4) involved six distinct steps in which only 40% of the atoms in the reactants ended up in the final product. Even if this reaction resulted in an impossible 100% yield, it would still mean that most of the atoms involved in the synthesis are incorporated into waste and by-products. This represents a poor result environmentally and economically.

In 1992, a new 'green' synthesis pathway was developed involving only three separate steps (Figure 12.1.4) in which 77% of the atoms from reactants resulted in the final product. This value can be further improved to around 99% by regenerating and reusing some reactants. It is estimated that the worldwide production of ibuprofen is around 15 000 tonnes per year. Using the brown synthesis, this would also mean at least 15 000 tonnes of waste and by-products, but by utilising the green synthesis, this unnecessary waste is avoided.

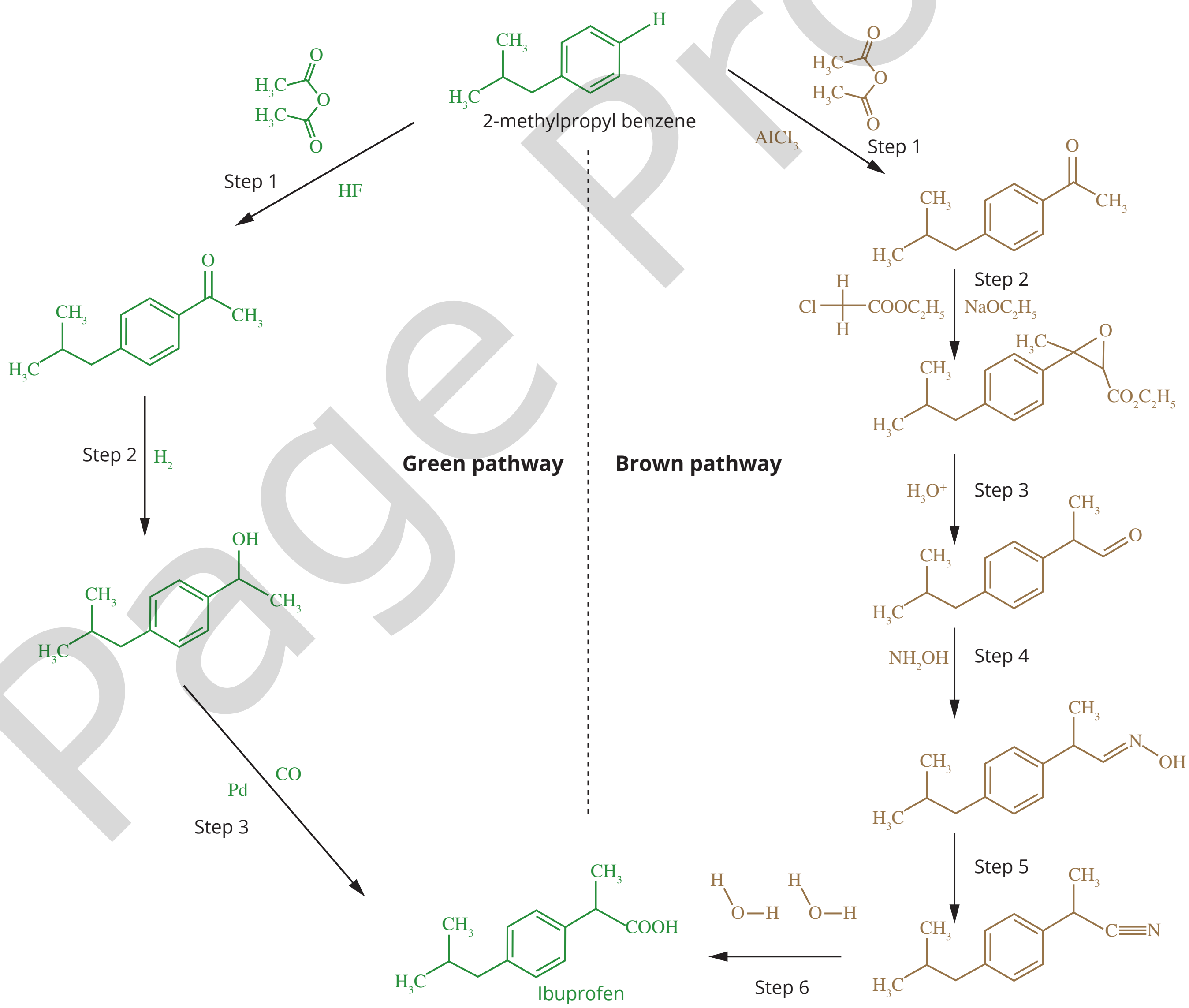


FIGURE 12.1.4 The older 'brown' and newer 'green' synthesis pathways for ibuprofen

EXTENSION

Atom economy

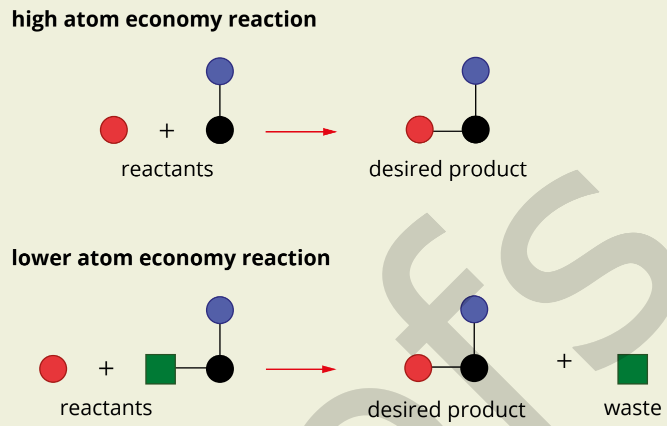


FIGURE 12.1.5 Examples of a high and low atom economy synthesis

Today, chemists follow the philosophies represented by green chemistry and endeavour to design reaction pathways with the maximum atom economy. The atom economy for a chemical reaction is a measure of how many of the atoms in the reactants end up in the desired product. As you can see in Figure 12.1.5, where the different coloured symbols represent atoms or groups of atoms, if the atom economy of a reaction is high, all or most of the atoms in the reactant molecules end up in the desired product molecule. If the atom economy of a reaction is low, fewer of the reactant atoms end up in the desired product. The atoms that don't end up in the desired product are waste products of the reaction.

Calculating the atom economy of a reaction provides a method of accounting for the use of materials in a manufacturing process. It tracks all the atoms in a reaction and calculates the mass of the atoms of reactants actually used to form products as a percentage of the total mass of reactants. From this, the mass of reactant atoms that end up as waste can also be calculated.

Once the balanced equation for a reaction is known, the atom economy can be calculated from the formula:

$$\text{Atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$

Since, in a chemical reaction, the total mass of products is equal to the total mass of reactants, this alternative formula can also be used:

$$\text{Atom economy} = \frac{\text{mass of desired product}}{\text{mass of all reactants}} \times 100$$

Use Worked Example 12.1.1 to help you with calculations of atom economy.

Worked example 12.1.1

CALCULATING ATOM ECONOMY

Calculate the atom economy for the production of ethanol from chloroethane. In this process, chloroethane is heated with a solution of sodium hydroxide. The equation for the reaction is:

$$C_2H_5Cl(aq) + NaOH(aq) \rightarrow C_2H_5OH(aq) + NaCl(aq)$$

Thinking	**Working**
Calculate the total molar mass of the reactants.	$M(C_2H_5Cl) + M(NaOH)$ $= [(2 \times 12.01) + (5 \times 1.008) + 35.45] + [22.99 + 16.00 + 1.008]$ $= 104.5\ g\ mol^{-1}$
Calculate the molar mass of the required product.	$M(C_2H_5OH)$ $= (2 \times 12.01) + (6 \times 1.008) + 16.00$ $= 46.07\ g\ mol^{-1}$
Calculate the atom economy for the reaction using the formula: $\text{Atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$	$\text{Atom economy} = \frac{46.07}{104.5} \times 100$ $= 44.1\%$ So in this process, only 44.1% of the starting materials are converted to the desired product. The remainder of the chemicals used is waste.

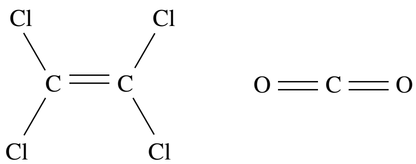
Worked example: Try yourself 12.1.1

CALCULATING ATOM ECONOMY

Calculate the percentage atom economy for the formation of 1-iodopropane ($CH_3CH_2CH_2I$) from propan-1-ol. The equation for the reaction is:

$$CH_3CH_2CH_2OH(aq) + NaI(aq) + H_2SO_4(aq) \rightarrow CH_3CH_2CH_2I(aq) + NaHSO_4(aq) + H_2O(l)$$

> A carcinogen is a substance capable of causing cancer in living cells.



perchloroethylene (PERC) carbon dioxide

FIGURE 12.1.6 Perchloroethylene (PERC) and carbon dioxide both have non-polar structures, which make them suitable for removing grease and oil.

> Hydrophobic substances are not attracted to, or will not mix homogenously, with water.

Green chemicals

The history of chemistry is littered with infamous chemicals such as tetraethyl lead in petrol and the insecticide DDT. Although effective in their chosen roles, these chemicals posed significant health and environmental dangers. One of the 12 principles of green chemistry is to use equally effective, but safer and preferably renewable, chemicals.

Chemists are constantly searching for new, innovative and environmentally friendly chemicals to replace long-used, but often less safe, chemicals. One chemical that has been commonly used in dry-cleaning is perchloroethylene (PERC). PERC is the most commonly used dry-cleaning solvent. It is responsible for the characteristic smell of freshly dry-cleaned fabrics and is a recognised likely carcinogen and has been linked with other health conditions such as Parkinson's disease.

As can be seen in Figure 12.1.6, PERC is perfectly non-polar, which makes it ideal for dissolving hydrophobic substances such as oil and grease. A commonly available alternative to PERC that is also perfectly non-polar is carbon dioxide (Figure 12.1.6). The only problem with using carbon dioxide as a solvent is that at room temperature it is a gas, which makes it less suitable as a cleaning solvent than PERC, which is a liquid at room temperature. Simply cooling carbon dioxide to a liquid would mean reducing the temperature to –80°C, a temperature that would likely damage delicate fabrics.

To solve this problem, chemists use what is known as supercritical carbon dioxide. This is carbon dioxide that at certain temperatures and pressures ($T > 31$°C and $P > 7.3$ MPa) demonstrates the properties of both a liquid and a gas at the same time. Using supercritical carbon dioxide with an appropriate detergent is an equally effective, yet significantly safer and environmentally friendly, alternative to perchloroethylene.

CHEMISTRY IN ACTION

Antibacterial handwashes—when soap became simply not enough

In the last few years, there has been a huge increase in the number of antibacterial handwashes and cleaning products (Figure 12.1.7) available to consumers. These handwashes are advertised as providing a greater level of protection from bacteria than simple soap and water. One of the major active ingredients in antibacterial products is triclosan.

FIGURE 12.1.7 Triclosan is the active ingredient in many antibacterial consumer products.

Triclosan (Figure 12.1.8) was developed in the 1960s and is an effective antibacterial and antifungal agent. However, a study carried out by the US Food and Drug Administration found no evidence that triclosan in soap provided any benefit compared with washing with regular soap and water.

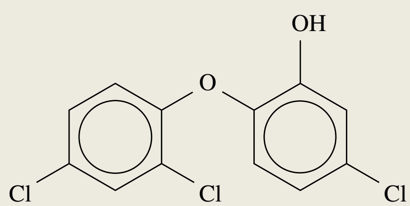


FIGURE 12.1.8 Triclosan is one of the major ingredients in antibacterial handwashes.

The potential adverse health effects of triclosan are still being investigated, but its impact on the environment is clear. In 2016, a study showed that the edible parts of plants that were irrigated with triclosan-contaminated water still contained triclosan months later. Triclosan primarily finds its way into the environment through sewage and waste waters. It is toxic to a range of aquatic bacteria and algae and has been detected in animals higher up the food chain, including fish and dolphins.

Numerous companies have voluntarily removed triclosan from their products in the face of mounting evidence of its environmental harm. Triclosan was banned for use in soap by the US Food and Drug Administration at the end of 2016 due to a lack of evidence of its efficacy. To date, triclosan is still legal in Australia.

Extracting gold in Western Australia

Gold mining (Figure 12.1.9) is the fourth largest commodity sector in Western Australia, valued at $10 billion each year. The industry standard method for gold extraction and refining involves gold cyanidation, where gold is leached from the ore as a water-soluble cyanide complex:

$$4Au(s) + 8CN^-(aq) + 2H_2O(l) + O_2(g) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

Leaching is the process of extracting certain substances from a solid by dissolving them in a liquid.

FIGURE 12.1.9 The Kalgoorlie super pit; the second largest open-cut gold mine in Australia after the Newmont Boddington gold mine

Once the gold is extracted by the carbon-in-pulp process, the tailings contain significant concentrations of cyanide, which is toxic. Often these waste streams are processed to detoxify them prior to storage, but processing does not completely eliminate the cyanide present in the tailings. Aqueous solutions of cyanide rapidly degrade in sunlight into harmless substances but the cyanide-related cyanates and thiocyanates, although less toxic, may persist in the environment for a number of years. This makes the processing and storage of gold-refining wastes an expensive exercise.

Chemists at Curtin University in Perth have developed a gold extraction process where the amino acid glycine, the simplest of the amino acids, is substituted cyanide (Figure 12.1.10). Glycine demonstrates a number of benefits over cyanide: it is environmentally benign, cheaper and recyclable. Because glycine is non-toxic, it drastically reduces the environmental danger that mine tailings represents. Glycine is as accessible as cyanide and, because it is far safer, it lends itself to *in situ* leaching, reducing the need for vast open cut mines like the Super Pit.

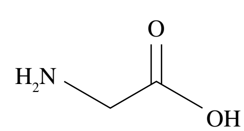


FIGURE 12.1.10 Glycine—the simplest amino acid—is being used in gold extraction.

CHEMISTRY IN ACTION

The 2014 Mount Polley mine disaster

Tailings are the materials left over after valuable minerals have been separated the from the ore. Tailings usually consist of a slurry of fine particles of uneconomical metals, minerals and chemicals. Historically, tailings were disposed of in the most convenient manner—dumping into nearby downstream running water such as rivers and streams. Today, tailings are often stored in large ponds or dams. The tailings are pumped into the ponds and sedimentation of the solids and evaporation of water is allowed to take place.

On 4 August 2014, there was a breach in a tailings pond at the Mount Polley copper and gold mine in British Columbia, Canada (Figure 12.1.11). This allowed 10 million cubic metres of waste water and 4.5 million cubic metres of tailings to pour into nearby Polley Lake. This spill raised the level of Polley Lake by 1.5 metres and the lake then emptied into the nearby Quesnel Lake.

According to the mining company's documents, 326 tonnes of nickel, more than 400 tonnes of arsenic, 177 tonnes of lead and 18400 tonnes of copper and their compounds were placed into the tailings pond in the previous year. Much of this will have ended up in the local environment, including lakes and streams.

This is often considered the biggest environmental disaster in modern Canadian history and the true extent of the damage to the environment is likely to remain unknown for years or decades to come.

FIGURE 12.1.11 The Mount Polley tailings dam breach caused much destruction in the local environment.

Waste minimisation and remediation

Producing large amounts of waste is not economically or environmentally sustainable. Industries spend a lot of money and time to optimise operations and reduce inefficiencies, including waste generation. The key financial losses associated with waste are two-fold. First, reagents that end up in wastes do not end up in marketable product. Second, treating and storing waste is expensive. Applying the principles of green chemistry is one way a company can improve their profitability through reducing costs related to waste treatment and disposal while at the same time reducing the environmental impact of their business and becoming more sustainable.

One way greener industries can be developed is to base a process on another industry's waste. This drastically reduces operating costs because businesses are usually happy to sell a waste that they would otherwise have to dispose of at an associated cost.

Chemical industries often locate themselves close to other industries on which they rely. This minimises material transport costs and allows several industries to make the most of existing infrastructure such as ports and rail networks. This synergy of industries is a common strategy aimed at increasing profitability but it can also be used to develop green chemistry solutions to treating waste products.

The contact process used to produce sulfuric acid needs a steady source of sulfur dioxide as its key starting material. This sulfur dioxide can be obtained by burning solid sulfur in air, or using waste sulfur dioxide from another industry. When sulfide ores are roasted, one of the waste products is sulfur dioxide, which, if released into the air contributes to environmental problems such as acid rain. The contact process is used south of Kalgoorlie to create sulfuric acid, a marketable product, from the nickel smelter's waste product.

One of the most significant waste products produced by the Alcoa aluminium refinery in Kwinana is 'red mud'. Red mud is the tailings produced after the extraction of alumina from bauxite ore and consists of a highly alkaline slurry of sediment particles and waste water. This red mud is pumped into tailings ponds (Figure 12.1.13) where it is left to dry through evaporation, and then the sediment is stored (dry stacking). Despite the washing of the tailings in the refinery, the red mud remains highly alkaline due to the bases used in the extraction process. This is the major obstacle in the disposal of the tailings as the high alkalinity poses a risk to surface and ground water resources.

FIGURE 12.1.13 The tailing ponds at Alcoa's Kwinana aluminium refinery. You can see the 'red mud', which is highly alkaline.

A collaborative exercise between the Alcoa aluminium refinery and the nearby CSBP ammonia plant has found a green chemistry solution to both their waste products. The hydrogen required in the Haber process is produced by steam reforming of methane. One of the by-products of this is carbon dioxide, a greenhouse gas. This carbon dioxide is then used to neutralise the high alkalinity of Alcoa's tailings in a process called carbonation. This reduces the pH of the tailings to levels closer to that of the surrounding soils, making the tailings safer to dispose of.

Rendering the waste product of an industry safe so that it can be disposed of makes a lot of sense environmentally, but not so much economically because this waste still needs to be disposed of at some cost. Economically, the ideal scenario would be to turn your waste product into a marketable commodity and have someone pay you for your waste.

CHEMFILE

Lobster is on the menu at UWA

FIGURE 12.1.12 Dr Mohamed Makha

Dr Mohamed Makha (Figure 12.1.12) and a team of researchers at the University of Western Australia have developed a new and environmentally friendly extraction process that turns discarded lobster shells into a valuable manufacturing material.

Chitin (pronounced ky-tin) is a long-chain polymer that is found throughout nature. It forms the cell walls of fungi and the exoskeletons of arthropods, including lobsters. It is used in a number of different industrial processes, from pharmaceuticals, to a food additive, to manufacturing biodegradable plastics.

The new extraction process utilises a new, renewable, environmentally friendly solvent and utilises energy-efficient microwaves as a heat source. What was once discarded from kitchens could be the basis for a new, green, manufacturing industry in Western Australia.

FIGURE 12.1.14 This farmer from the Peel region is holding a lump of Alkaloam that was spread on his paddocks.

The fine-grained tailings residue produced after the carbonation process has found use as a beneficial soil additive known as Alkaloam (Figure 12.1.14). Alkaloam provides a number of benefits to a typical sandy Perth soil, including raising the pH and increasing phosphate retention by up to 70%. It has been shown that Alkaloam is safe to use on grazing land used by livestock and has found particular use in treating another environmental problem in the Peel–Harvey estuary.

The Peel–Harvey estuary has become eutrophic; that is, it experiences low oxygen levels due to rapid plant and algae growth resulting from increased nutrient concentrations in its waters (Figure 12.1.15). The surrounding Peel–Harvey catchment area contains a large horticultural industry that applies fertilisers to the soil as part of its operating procedure. Perth's sandy soils are typically very poor at retaining nutrients, particularly phosphates, which leach from the soils into the Peel–Harvey estuary, contributing to the eutrophication problem. The application of Alkaloam to nearby farmland is seen as a viable method of preventing a large portion of the applied phosphate fertilisers from ending up in the estuary, thus reducing the eutrophication problem.

Eutrophication is the accelerated growth of plants and algae in water as a result of elevated nutrient levels.

FIGURE 12.1.15 Algal blooms form as a result of eutrophication.

The term 'waste' does not only apply to physical materials produced by the process; it also applies to energy liberated by reactions. The central reaction in the Haber process is exothermic; simply liberating the vast quantities of heat generated by this reaction into the air is another form of waste. The heat removed in condensing the ammonia produced at the end of the process is used to heat the feed gases of hydrogen and nitrogen. In this way, the heat energy is recycled, avoiding the need for the plant to use additional energy to generate more heat, saving both the environment and money.

EXTENSION

A green future for WA

Two of the key chemical products in Western Australia are ammonia and sulfuric acid. These are economically important industries that other industries rely upon.

Ammonia is produced by the Haber process in the Pilbara, Sulfuric acid is produced by the contact process in Kalgoorlie. These two industries intersect at the CSBP fertiliser plant in Kwinana where they are used to manufacture ammonium sulfate according to the reaction:

$$2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

You can compare the environmental impact and sustainability of the manufacture of the reagents used by each of these processes and suggest changes that could be made to each process through the application of green chemistry principles.

You could consider:

- the environmental impact of how the reagents are sourced, including wastes generated
- any existing examples of how green chemistry has been applied to the processes
- any possible alternative sources for the reagents and their comparable environmental impact
- the atom economy of the syntheses used.

12.1 Review

SUMMARY

- Green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.
- The philosophy of green chemistry is underpinned by 12 principles.
- The chemical method used to convert starting reagents to product is known as the synthesis of the product.
- Atom economy is a measure of the proportion of atoms from the reagents that end up in the desired product.
- The application of the principles of green chemistry should not have to come at significant economic cost.

KEY QUESTIONS

1 What is green chemistry?

2 How is green chemistry different from environmental chemistry?

3 What are some ways chemists can make a synthesis ‘greener’?

4 Why is using renewable materials important?

5 Why would the new ibuprofen synthesis (shown in Figure 12.1.4) be as, if not more, profitable than the old one?

6 Why would water not be a suitable replacement for perchloroethylene as a dry cleaning solvent?

7 What are the advantages of using glycine as a leaching agent over cyanide for metal extraction?

8 Suggest other ways to reduce the eutrophication in the Peel–Harvey estuary.

Chapter review

12

KEY TERMS

green chemistry
renewable
sustainable
synthesis

Green chemistry

1 Which of the following is an aim of green chemistry?
  A Design chemical processes that maximise profits.
  B Design new chemicals.
  C Learn about the chemical processes that occur in the natural environment.
  D Design safer chemical products and processes and reduce or eliminate the generation of hazardous substances.

2 Which of the following is not a principle of green chemistry?
  A Use less energy.
  B Reduce the risk to people and the environment.
  C Avoid using artificial chemicals.
  D Prevent or reduce waste.

3 True or false? Under green chemistry philosophy, industries must sacrifice profits in order to become greener.

4 Considering the philosophy of green chemistry, which of the following alternatives is the best?
  A Turn your waste product into a profitable commodity.
  B Avoid any waste.
  C Dispose of waste responsibly.
  D Store waste in tailing ponds.

5 True or false? Organic farming is always an example of green chemistry.

6 What attributes would be required for an alternative chemical synthesis to be considered a 'green' synthesis?

7 Why could changing to a 'greener' chemical synthesis make good economic sense for a company?

8 Why is the use of catalysts integral to green chemistry?

9 How can using locally sourced resources reduce the environmental impact of an industrial process?

10 In many industries in the past, waste materials were simply incinerated. What possible environmental impacts would this have had?

11 How can you, as a student, ensure your laboratory experiments are 'green' experiments and reduce their environmental impact?

12 Use the MSDSs of carbon dioxide and perchloroethylene to compare the associated health risks of each.