

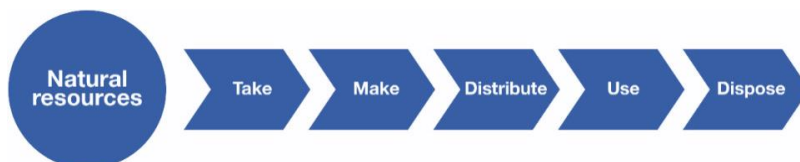
Green Chemistry

Green Chemistry principles particularly relevant to the study of VCE Chemistry.

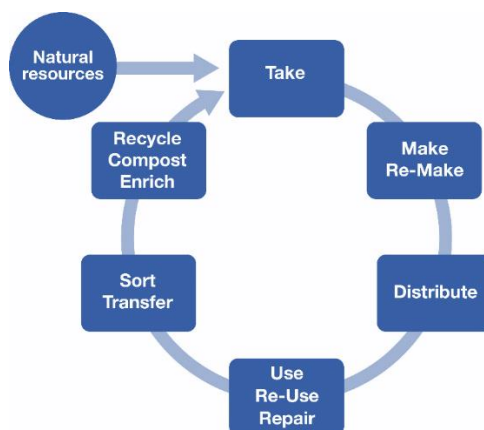
- **Atom economy:** Processes/pathways should be designed to maximise incorporation of all reactant materials used in the process into the final product.
- **Catalysis:** Catalysts should be selected to generate the same desired product(s) with less waste and using less energy and reagents in reaction processes/pathways.
- **Design for degradation:** Chemical products should be designed so that at the end of their use they break down into harmless degradation products and do not persist in the environment.
- **Design for energy efficiency:** Processes/pathways should be designed for maximum energy efficiency and with minimal negative environmental and economic impacts.
- **Designing safer chemicals:** Chemical products should be designed to achieve their intended function while minimising toxicity.
- **Prevention of wastes:** It is better to prevent waste than to treat or clean up waste after it has been produced.
- **Use of renewable feedstocks:** Raw materials or feedstocks should be made from renewable (mainly plant-based) materials, rather than from fossil fuels, whenever practicable.

Linear and circular economies

Linear economy: Operates on a 'take-make-dispose' model, making use of resources to produce products that will be discarded after use. A simple representation is shown below.



Circular economy: A continuous cycle that focuses on the optimal use and re-use of resources from the extraction of raw materials through to production of new materials, followed by consumption and re-purposing of unused and waste materials. A simple representation is shown below.



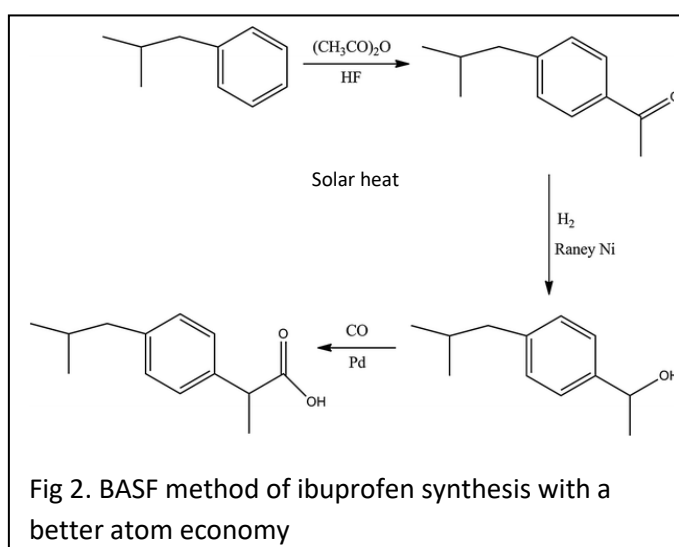
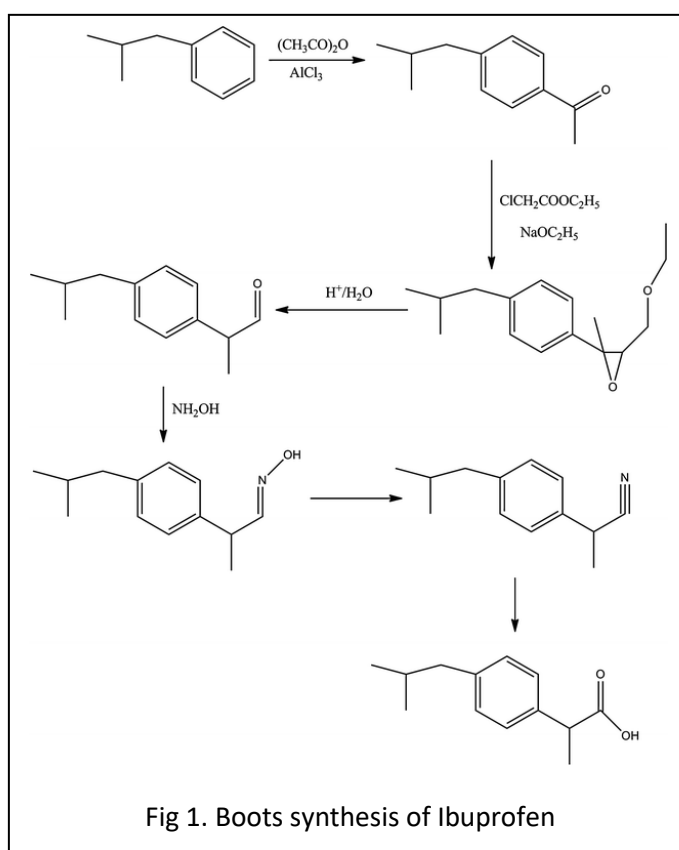
Example 1 - Synthesis of ibuprofen

Synthesis of pharmaceutical products requires a great deal of heat, traditionally supplied by fossil fuels. In recent times a push to implement more renewable energy sources, such as, solar heat, into the production process has been made to generate more sustainable production methods.

Ibuprofen is a nonsteroidal anti-inflammatory drug that is commonly used worldwide for pain relief and fever/inflammation reduction. It was discovered in the 1960s by Andrew Dunlop, who initially tested the drug on cures for hangovers. The drug was first made available via prescription in 1974 in the United States and soon became available as an over the counter drug.

The original synthetic process, fig 1, known as the Boots synthetic process, involved several complicated steps that generated a considerable amount of chemical waste. Each step in this process often requires cooling, isolation, and purification, followed by reheating for the next step this makes this procedure energy intensive. Since this method of industrial production generated an enormous amount of waste, an alternative synthetic route was necessary. The original method of synthesising ibuprofen consisted of several environmentally hazardous reagents, such as hydrazine, hydroxylamine and aluminium chloride. Hydrazine must be handled with care since it can explode upon heating. Hydroxylamine is also absorbed through the skin causing cellular mutations.

In 1992, an alternative process of synthesizing ibuprofen (Fig. 2) that was much more environmentally friendly and a model of "atom economy" was unveiled. This procedure is now owned by BASF and is used as the synthetic procedure for the production of this pharmaceutical. Reagents that are commonly listed as irritants are still used in this pathway (aluminum chloride, acetyl chloride) The reagent



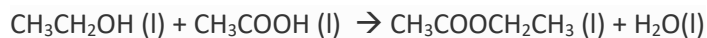
that poses the most environmental/health concerns throughout this process is hydrazine. Hydrazine is a highly toxic, corrosive liquid that has several adverse health effects. However, in the green chemistry process shown in fig 2, hydrazine is replaced by hydrazine hydrate. The hydrate form is still considered to be hazardous upon human contact, but health hazards are greatly reduced when compared to hydrazine. In the green chemistry pathway (fig 2) the toxic AlCl_3 catalyst is replaced with a less hazardous and recyclable catalyst, HF. Recycling HF involves capturing the vaporized HF after the reaction, condensing it, and then reintroducing it into the reaction mixture.

Using the synthesis of ibuprofen as an example, complete the table below

Green Chemistry principle being applied	Original synthesis process	Green Chemistry modifications

Example 2 - Synthesis of ethyl acetate

Ethyl acetate is used widely in industry as an organic solvent. The reaction is given below.



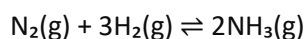
The traditional method of producing ethyl acetate involves ethanol and acetic acid as the raw materials and concentrated H_2SO_4 as the catalyst. Sulfuric acid is a strong acid that poses significant risks if it gets into water ways via accidental spills. The synthesis of sulfuric acid ([Contact process](#)) is a major contributor to atmospheric SO_2 . SO_2 will react with water vapour to form acid rain which causes significant deforestation and acidification of waterways. High temperatures are also a key feature of the production of sulfuric acid and the heat energy is primarily provided by the burning of sulfur to produce SO_2 . Final purification of the ethyl acetate ester involves the neutralization of sulfuric acid with a strong base (NaOH) and final distillation. Overall, this process requires strong acids and bases and is energy intensive.

The green chemistry pathways involves the use of solid state acid catalysts (zeolite) with obvious advantages of ease of purification. Solid catalysts can be filtered and reused. These solid states are so efficient that high temperatures are often not necessary.

Using the synthesis of ethyl acetate as an example, complete the table below

Green Chemistry principle being applied	Original synthesis process	Green Chemistry modifications

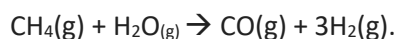
Example 3 - Synthesis of ammonia



Globally, agriculture depends on industrial nitrogen fertilizer to improve crop growth. Fertilizer production depends on the synthesis of ammonia and consumes large amounts of fossil fuels thus contributing to global warming. The traditional method of ammonia production is via the Haber-Bosch method. This method requires:

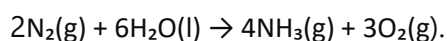
- High temperatures (400 – 650°C)
- Iron based catalysts that require the presence of aluminium oxide.
- High pressure of between 200 and 400 atmospheres.

The nitrogen from the reaction is obtained from the atmosphere whilst the hydrogen gas is obtained largely from a process called steam reformation that requires natural gas as a feedstock.



Industrial production of ammonia via the Haber-Bosch method is one of the most energy intensive and CO₂ producing processes.

Research into electrochemical synthesis of ammonia is taking place currently



This process takes place at ambient temperature and pressure. Research is looking at potential solutions such as harnessing nitrogenases—enzymes capable of converting atmospheric nitrogen N₂ to NH₃ in ambient conditions. It is therefore a major goal of synthetic biology to engineer functional nitrogenases into crop plants, or bacteria that form symbiotic relationships with crops, to support growth and reduce dependence on industrially produced fertilizer.

Using the synthesis of ammonia as an example, complete the table below

Green Chemistry principle being applied	Original synthesis process Haber-Bosch	Electrochemical synthesis