Chem Factsheet

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General Principles of Green Chemistry

Introduction

The scientific and technological advances made in the past two centuries have revolutionised humanity. Advances in transportation, communication, medicine and food-production have led to unprecedented increases in human populations and increasing demands on natural resources. The negative effect of progress is observed in rising levels of pollution and in the destruction of local ecosystems. Scientists have discovered holes in the protective ozone layer in the stratosphere. They continue to link the increased use of chemicals to cancers and other adverse human and environmental health outcomes. Vital ocean ecosystems are under threat by tonnes of plastic waste.

By the late twentieth-century, many governments had begun actively regulating the generation and disposal of industrial waste. In Europe, the European Environment Agency (EEA) was established in 1990 to provide independent information on the environment, including air and climate, nature, sustainability and well-being, and economic sectors.

Green chemistry is a branch of chemistry that focuses on producing safer and resource-efficient materials and processes. This requires developing technological solutions that address the consumption of non-renewable resources and issues related to the production of hazardous materials. In 1998, Paul Anasta and John C. Warner established twelve principles for conducting green chemistry. These guiding principles consider the efficiency of chemical processes, identifying renewable chemical feedstocks and energy sources, and utilising, whenever possible, benign materials. This technological approach distinguishes green chemistry from another branch of chemistry, environmental chemistry, which studies the effects of chemicals on nature, e.g. pollution.

Twelve principles of green chemistry

Waste Prevention

The production of hazardous waste materials in chemical processes detrimentally impacts the environment and can be expensive to clean up. This first principle of green chemistry argues it is better to develop chemical processes that minimise the hazardous waste produced at each step of the process. An example is in the production of polystyrene foam. Historically, chlorofluorocarbons, CFCs, have been used as blowing agents. CFCs are recognised as ozone depleting chemicals and the release of CFCs into the atmosphere is a serious environmental hazard. The replacement of CFCs with supercritical carbon dioxide (i.e. carbon dioxide in a fluid state above its critical temperature and critical pressure) allows the polystyrene foam to be recycled more easily and more safely. The carbon dioxide is recycled, resulting in no net increase of carbon dioxide.

Atom Economy

Chemical processes should be designed to incorporate as much of the raw materials used into the final product. This decreases the amount of waste materials produced and improves the efficiency of the manufacturing process. A process converting all reactant atoms into the final product or products has a 100% atom economy.

Key Fact:

Atom economy is a measure of the atoms wasted in a chemical reaction or process. To calculate atom economy:

$$\text{atom economy} = \frac{\text{molecular mass of desired product or products}}{\text{sum of the molecular mass of all reactants}} \times 100$$

If a chemical reaction produces by-products, then it is necessary to develop chemical processes that will either eliminate these by-products, or, ensure the by-products are as limited and as harmless as possible. For example, the Olin Raschig process uses sodium chlorate(I), NaClO, to oxidise ammonia, producing hydrazine, sodium chloride and water.

$$2NH_3 + NaClO \rightarrow N_2H_4 + NaCl + H_2O$$

Replacing the more hazardous sodium chlorate(I) with the greener oxidising agent, hydrogen peroxide, H_2O_2, improves the atom economy of the reaction.

$$2NH_3 + H_2O_2 \rightarrow N_2H_4 + 2H_2O$$

Less hazardous

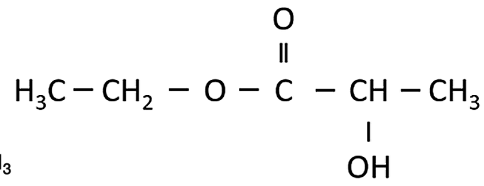
Chemical synthesis routes should be designed to be as safe as possible with due consideration given to the hazards of reactants used, the handling of intermediate substances, and potential waste materials. That is, to generate materials with little or no toxicity. This includes using green solvents, such as supercritical-CO_2, or using aqueous hydrogen peroxide to complete clean oxidation reactions.

Designing safer chemicals

Chemists can design molecules with a better understanding of their physical properties, toxicity and their potential impact on the environment. This includes the engineering of biological systems to develop biocatalytic processes. These reduce the need for hazardous materials and subsequent damage to the environment, and increases the efficiency of chemical processes.

Safer solvents

Most chemical processes use large quantities of solvents and separating agents. These materials contribute significantly to the waste materials produced. Solvents are also used for cleaning and degreasing. Many solvents used are chlorinated and toxic, creating potential human health issues and environmental hazards. Green chemistry has led to the development of green solvents. These are materials derived from renewable sources and will biodegrade to naturally occurring, and safe, substances. Ethyl lactate, which is derived from processing corn, is an example of a green solvent. Lactate esters are used as solvents in paints and in coating materials for wood, metals and plastics. They are non-corrosive, non-carcinogenic and non-ozone depleting. They are also biodegradable and easy to recycle.



Ethyl Lactate,
$C_2H_5OCOCH(OH)CH_3$

Energy efficiency

Green chemistry technology leads to developing chemical processes that work close to ambient conditions. This reduces the need to heat or cool reactions, or using pressurised vessels or vacuums. This reduces energy requirements, leading to positive economic and environmental impacts.

Renewable feedstocks

The reliance on non-renewable sources, such as petrochemicals, has encouraged the chemical industry to shift to sourcing materials from renewable sources, that is, plant-based. The conversion of bio-materials into useful chemicals are low-energy, low-toxic pathways and essentially carbon-neutral processes (i.e. there is no net increase in carbon dioxide). Other approaches use genetically-modified bacteria to carry out complex synthesis using established metabolic pathways. The bacteria can be grown quickly and fed with renewable, plant-derived, feedstock.

Reduce derivatives

Chemical processes should reduce the requirement for derivatization, that is, steps involving temporary modifications, or providing protection or deprotection groups. Decreasing the number of steps in a chemical process reduces the amount of materials consumed in the reactions, and will reduce the amount of waste materials generated.

Catalysts

Selecting appropriate catalysts for reaction steps increases reaction rates, lowers energy demands and may improve atom economy (e.g. Monsanto and Cativa processes). Catalysts can increase selectivity and minimise waste. Selective catalytic reagents are preferable to stoichiometric reagents.

Design for degradation

Green chemistry technologies involve designing substances that easily degrade into non-hazardous materials. The benefits of producing non-toxic materials, with non-toxic degraded products, is in the ease of disposal, reducing the cost of waste treatment and harmful impacts to the environment.

Pollution prevention

Green chemistry technologies are developing analytical methods that allow the real-time monitoring and control of hazardous materials. This prevents the formation and possible release of pollutants during the reaction processes.

Accident prevention

The design of chemical processes should minimise the potential for chemical accidents, including the accidental release of chemicals and/or explosions. This requires detailed identification and assessments of the potential risks involved in each step of a chemical process.

Green chemistry and pharmaceuticals

The pharmaceutical industry continues to develop and implement green chemistry technologies. This includes massively reducing the use of chlorinated and highly-volatile solvents in drug manufacturing processes. Traditional solvents, such as: ethoxyethane, $C_2H_5OC_2H_5$; dichloromethane, CH_2Cl_2; and propanone, CH_3COCH_3, have been largely replaced with water, H_2O, 2-methylbutan-2-ol, $CH_3C(CH_3)(OH)CH_2CH_3$, and ethyl ethanoate, $CH_3COOC_2H_5$. It is estimated that over half of the chemicals used in the pharmaceutical industry are solvents. Green chemistry technologies are used to reduce the amounts of solvents used, replace hazardous solvents with less hazardous ones, and recover solvents that have a high environmental impact, rather than relying on incineration. The increased use of biocatalytic processes in chemical and pharmaceutical synthesis has allowed for the replacement of non-aqueous solvents with water, improving the environmental impacts of these production processes.

Green chemistry and food production

The use of supercritical-CO_2 generally requires higher start-up costs. However, supercritical-CO_2 tends to produce high quality products, offsetting the increased investment required. Supercritical-CO_2 is increasingly used in the food industry. It is used in decaffeination processes, to remove fats to produce low-fat varieties, and is used in the extraction of flavours and fragrances.

Enzymatic processes have been developed for the interesterification of oils and fats, leading to the elimination of trans-fats in commercially prepared foodstuffs. Trans-fats are considered as having adverse effects to human health. As well as producing trans-fat free food, enzymatic processes have reduced the use of toxic chemicals and the amount of waste by-products.

Butanedioic acid (Saccinic acid), $(CH_2)_2(CO_2H)_2$, is an important platform chemical. These are compounds used across a broad range of chemical processes to produce different substances. Butanedioic acid is a food additive and is taken as a dietary supplement. It is also used as an acid regulator in the food and drink industry, i.e. to control acidity, as a flavouring agent, and in the commercial productions of polymers, resins, and solvents. Globally, up to 30,000 tons of butanedioic acid are produced every year, historically from petroleum-based feedstocks. Green chemistry technologies have developed processes that produce butanedioic acid from renewable feedstocks that are economically favourable and produce less waste materials.

Challenges to green chemistry technologies

There are economic obstacles to the implementation of green chemistry technologies. The cost of replacing plant equipment in bulk chemicals production presents commercial challenges for chemical companies. Developing new, expensive processes must accommodate the necessary economic improvements to warrant the investment required. Tackling environmental issues identified in chemical processes and manufacture are often viewed as inconvenient and costly. However, there are notable successes. Green chemistry technologies have helped remove toxic lead additives from petrol, acid-rain producing sulphur impurities from fossil fuels, and continues to develop safe, degradable replacements for CFCs. The continued benefits of applying green chemistry technologies depends on developing new scientific knowledge, and the political will of governments to tackle increasing environmental issues.

Questions

1) List the 12 Principles of Green Chemistry.
2) What is the difference between Environmental Chemistry and Green Chemistry?
3) Read through the following statements.

   Which statements uphold the 12 Principles of Green Chemistry?

   a) The release of substances into the environment must adhere to agreed standards or guidelines in terms of the amount released, or the concentration levels released.
   b) The energy required for a given process should be minimised in terms of its environments and economic impacts.
   c) Environmental benefits of green chemistry include cleaner production technologies and reduced emissions.
   d) Waste materials should be treated prior to release, or immediately after release, to lessen its risks to the environment.
   e) Design of chemical processes should seek to replace stoichiometric reagents with selective catalytic reagents.
   f) Chemical processes should be designed to maximise profits through the efficient use of energy and raw materials.
   g) Reaction steps in chemical processes should be designed to involve substances that have no, or little, toxicity and adverse effects on the environment.
   h) A key challenge to green chemistry is knowing when to reduce and eliminate hazardous waste.
   i) Chemical feedstocks and other raw materials should be renewable, instead of depleting.
   j) Chemical processes are best served through enduring to national standards applied to chemical facilities, supported by frequent inspections.

4) Select the green solvents from the list of solvents provided below:

   benzene, water, tetrachloromethane, ethanol, supercritical-CO_2, dichloromethane, 1-butanol, ethyl ethanoate.

Answers

1) (1) Waste prevention, (2) Atom economy, (3) Less hazardous chemical synthesis, (4) Designing safer chemicals, (5) Safer (Green) solvents, (6) Energy efficiency, (7) Renewable chemical feedstocks, (8) Reduce derivatives, (9) Catalysts, (10) Design for degradation, (11) Pollution prevention, (12) Accident prevention.
2) Environmental Chemistry tackles environment problems and seeks to protect the natural environment, i.e. addresses environmental issues after they have occurred.

Green chemistry seeks to develop technologies to eliminate chemical processes adversely impacting the environment, i.e. deals with issues, rather than the consequences after the fact.

3) The statements supporting the 12 Principles of Green Chemistry:

   c) Environmental benefits of green chemistry include cleaner production technologies and reduced emissions.
   e) Design of chemical processes should seek to replace stoichiometric reagents with selective catalytic reagents.
   g) Reaction steps in chemical processes should be designed to involve substances that have no, or little, toxicity, and adverse effects on the environment.
   h) A key challenge to Green Chemistry is knowing when to reduce and eliminate hazardous waste.
   i) Chemical feedstocks and other raw materials should be renewable, instead of depleting.

4) Water, ethanol, supercritical-CO_2, 1-butanol, ethyl ethanoate.

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