



Comprehensive Review on Green Chemistry: Challenges and Its Applications in Daily Life

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ABSTRACT

Green chemistry, often also termed sustainable chemistry (benign chemistry), is the formal descriptor behind every effort to make chemical reactions and/or processes environmentally benign. The reduction and, finally, the elimination of hazardous substances and solvents is a great challenge because it requires that many classic chemical reactions have to be re-formatted and, in some cases, entirely re-invented. Green chemistry is the use of chemistry techniques and methodologies that diminish or abolish the use or generation of feedstock, products, by-products, solvents, reagents, etc. that is hazardous to human health or the surroundings. Applying the concept of green chemistry in education is built on understanding the needs of pharmaceutical industries, educational institutions, and laboratories that have an important role in pharmacy to achieve good manufacture products.

Keywords: Green chemistry, waste disposal, hazardous, benign chemistry, novel reactions.

INTRODUCTION

Earth's resources are limited, and in order for mankind to survive, future generations must be left with enough resources to sustain basic living necessities. Our future challenges in the resource, environmental, economic, and societal sustainability demand more efficient and benign scientific technologies for working with chemical processes and products. With the increasing concerns about environmental protection, the synthesis of organic compounds from raw materials through a Green chemistry procedure is desirable.

Definition

The term Green chemistry¹ is defined as “The invention, design, and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances”. Green chemistry addresses such challenges by inventing novel reactions that can maximize the desired products and minimize by-products, designing new synthetic schemes and can simplify operations in chemical productions, and seeking greener solvents that are inherently environmentally and ecologically benign. Green chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and application of chemical products.

Green chemistry is commonly presented as a set of twelve principles proposed by Anastas and Warner. The principles comprise instructions for professional chemists to implement new chemical compounds, new syntheses, and new technological processes.

Twelve principles of green chemistry:

1. Prevention

As like the old saying “prevention is better than cure”. It is better to prevent before the waste is created than to

clean up. To minimize the generation of hazardous waste is an important step in the prevention of pollution. One could say that sustainability is the goal and green chemistry is the means to achieve it.

Ex: Use of solvent- less sample preparation techniques.

2. Atom economy

The atom utilization, atom efficiency or atom economy, first introduced by Trost. It is extremely useful for rapid evaluation of the amounts of waste that will be generated by alternative processes. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. Atom efficiency can be calculated by dividing the molecular weight of the desired product to the molecular weight of all substance formed.

$$\text{Atom efficiency} = \frac{\text{Molecular weight of desired product}}{\text{Molecular weight of all substances formed}}$$

The atom efficiencies of stoichiometric CrO_3 vs. catalytic O_2 oxidation of a secondary alcohol to the corresponding ketone are compared below is shown in the figure 1.

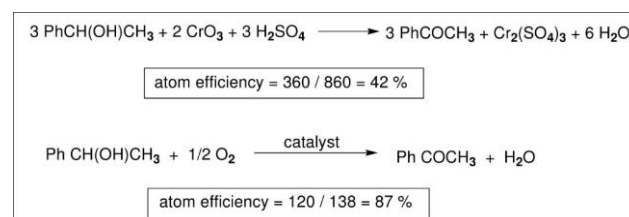


Figure 1: Atom efficiency of stoichiometric CrO_3 vs catalytic O_2 oxidation of an alcohol.

An interesting example of E factors and atom economy is the manufacture of phloroglucinol. In fact, it was produced from 2,4,6 - trinitrotoluene (TNT) is shown in the figure 2. It is a perfect example of nineteenth-century



organic chemistry. This process has an atom efficiency of less than 5 % and an E factor of 40, that is to say it normally generates 40 kg of solid waste, containing $\text{Cr}_2(\text{SO}_4)_3$, NH_4Cl , FeCl_2 and KHSO_4 per kg of phloroglucinol (water is not included) and clearly belongs in a museum of industrial archeology. Atom economy of ethylene oxide manufacture is shown in the fig 3.

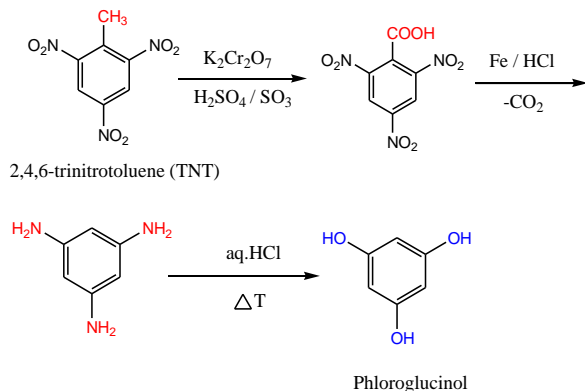
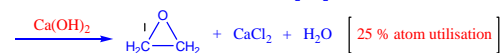


Figure 2: Phloroglucinol from 2,4,6- trinitrotoluene (TNT).

1. Chlorohydrin process



2. Direct Oxidation

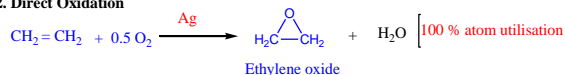


Figure 3: Atom economy of ethylene oxide manufacture.

3. Less hazardous chemical synthesis

Synthetic methodologies should be developed to produce or generate products which are less toxic to the environment² and humans. Some toxic chemicals are to be replaced with safer chemicals for green technology.

Ex: Adipic acid synthesis by oxidation of cyclohexene using hydrogen peroxide.

4. Designing safer chemicals

Safer chemicals should be designed while minimizing the toxicity. Chemists are molecular designer they design new molecules and new materials. Green chemists should make sure that the things that we make not only do what they're supposed to do, but they do it safely. This means that it's not only important how chemists make something, it's also important that what they make.

Ex: New less hazardous pesticide (E.g. Spinosad).

5. Safer solvents and auxiliaries

Unnecessary use of auxiliary substances should be avoided wherever possible and made harmless when used.

Ex: Supercritical fluid extraction, synthesis in ionic liquids.

Green solvents

Solvents are consumed in huge quantities in many chemical synthesis as well as for cleaning and degreasing. Traditional solvents are often chlorinated or toxic. Green solvents, on the other hand, are generally derived from renewable resources and biodegrade to harmless, often a naturally occurring product. Green solvents like as water, ionic liquids, liquid polymers, bio-ethanol, ethyl lactate, and supercritical fluids. The pharmaceutical industry has made important efforts towards identifying organic solvents with the reduced ecological footprint as compared to traditional reactions. Results of all-inclusive framework demonstrated by Capello et al on twenty-six organic solvents have shown that simple alcohols such as methanol or ethanol or alkanes like heptane and hexane are environmentally preferable solvents, whereas the use of dioxane, acetonitrile, acids, formaldehyde, and tetrahydrofuran are not recommendable results of another case study indicate that methanol-water or ethanol-water mixtures are environmentally favorable compared to pure alcohol or propanol - water mixtures. In fact, the solvent selection guide is shown in table 1.

Table 1: Solvent selection guide
Solvent selection guide

Pentane	Cyclohexane	Water
Hexane(s)	Toluene	Acetone
Di-isopropyl ether	Methylcyclohexane	Ethanol
Dichloromethane	TBME	2-Propanol
Chloroform	Isooctane	1-Propanol
NMP	Acetonitrile	Heptane
DMF	2-MeTMF	Ethyl acetate
Pyridine	THF	Isopropyl acetate
DMAc	Xylenes	Methanol
Dioxane	DMSO	MEK
Diemthoxyethane	Acetic acid	1-Butanol
Benzene	Ethylene glycol	t-Butanol.
Carbon tetrachloride		

6. Design for energy efficiency

Energy is not only expensive – most of the time the power plant that creates the energy contributes to pollution. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure

Ex: Polyolefin- polymer alternatives to PWC (polymerization may be carried with lower energy consumption).

7. Use of renewable feed stocks

The Green chemistry³ of polymers with degradable products and bio-based plastics are considered in the right direction for sustainability in the polymer field. There are several promising markets for biodegradable polymers such as polylactide. Plastic bags for household biowaste, barriers for sanitary products and diapers, planting cups, disposable cups, and plates are some typical applications

Ex: Production of surfactants.



8. Reduce derivatives

Unnecessary derivatization (use of blocking groups, protection, and temporary modification of physical/chemical processes) should be minimized to avoid the use of additional reagents and can generate waste.

Ex: On- fiber derivatization vs. derivatization in solution in sample preparations.

9. Catalysis

Catalysis is used in a reaction to minimize the energy requirements and is also used to increase the rate of the reaction. If the green catalyst is used it will have no toxicity.

Ex: Efficient Au (III) - catalyzed synthesis of β -enaminones from 1,3-dicarbonyl compounds and amines.

Catalytic C-C bond formation

Hoechst-Celanese process for the manufacture of the analgesic, ibuprofen, with an annual production of several thousand tons. In this process, ibuprofen is produced in 2 catalytic steps first one is hydrogenation second one carbonylation starting from p-isobutyl acetophenone with 100% atom efficiency. This process replaced a more classical route with involved more steps and a much higher E factor. Hoechst-Celanese process for Ibuprofen is represented in the fig 4.

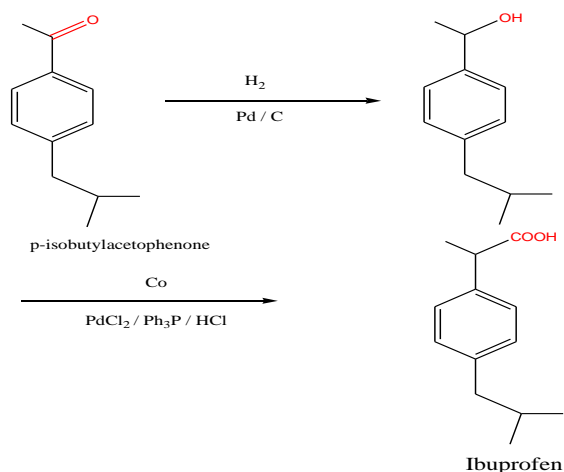


Figure 4: Hoechst-Celanese process for Ibuprofen.

Hoffmann-La Roche for the antiparkinson medication, lazabemide which is intended to treat and relieve the symptoms of parkinson's disease. This drug act by either increasing dopamine activity or reducing acetylcholine activity in the central nervous system. Palladium-catalyzed amidocarbonylation of 2,5- dichloropyridine replaced an original synthesis that involved 8 steps, starting from 2- methyl-5-ethylpyridine, and had an overall yield of 8 %. The amidocarbonylation route affords lazabemide hydrochloride in 65 % yield in a single step, with 100% atom efficiency. Two routes of lazabemide synthesis is shown in the fig 5.

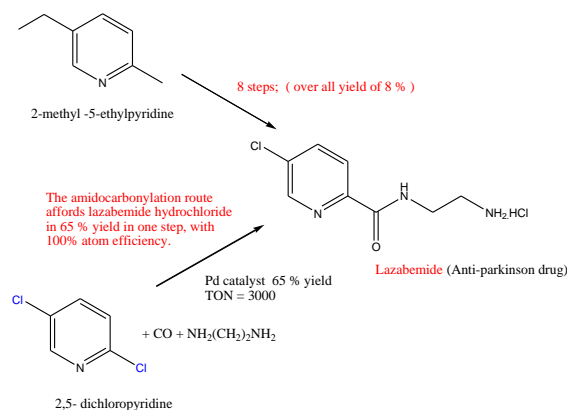


Figure 5: Two routes of Lazabemide synthesis.

10. Design for degradation

Chemical products should be designed so that at the end of their function they break down into benign degradation products and do not continue in the environment.

Ex: Synthesis of biodegradable polymers.

11. Real-time analysis for pollution prevention

Analysis of active pharmaceutical ingredients (APIs) and drug products, purity determination, enantiomer separation, all rely on methodologies either newly developed or specified by regulatory agencies. Impurities that arise from various steps during synthesis, manufacture, storage or transportation must be characterized and quantified. All requirements related to Green Analytical Chemistry must be also fulfilled in pharmaceutical analysis, with special attention.

Ex: Use of in-line analyzers for wastewater monitoring.

12. Inherently safer chemistry for accident prevention

Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Ex: Di-Me carbonate (DMC) is an environmentally friendly substitute or dimethyl sulfate and methyl halides in methylation reaction.

There are so many examples and applications of green chemistry⁴⁻⁶ for example as starting materials (polysaccharides polymers, commodity chemicals from glucose), green chemical reactions (atom economy and homogeneous catalysis, halide free synthesis of aromatic amines), as green reagents (Green oxidative transmission complexes, liquid oxidation reactor, non phosgene isocyanate synthesis), as green reagents (green oxidative transmission complexes, liquid oxidation reactor, non phosgene isocyanate synthesis). Green solvent and reaction conditions, green chemical products (design of alternative nitrites, donlar's polyaspartic acids, polaroid's complexed developers), Manufacture of drugs (oligonucleotide drugs), In agriculture (management of

the soybean cyst nematode by using a biorational strategy, potential of entomo-pathogenic fungi as biological control agents against the formosan subterranean termite). No reaction can be perfectly

green. The overall negative impact of chemistry research and the chemical industry can be reduced by implementing the twelve principles of green chemistry wherever possible is shown in table 2.

Table 2: The twelve principles of green chemistry

S.No	Principle	Examples
1.	Waste Prevention	Use of solvent- less sample preparation techniques.
2.	Atom Economy	Hydrogenation of carboxylic acids to aldehydes using solid catalysts.
3.	Less hazardous chemical synthesis	Adipic acid synthesis by oxidation of cyclohexene using hydrogen peroxide.
4.	Designing safer chemicals ⁷	New less hazardous pesticide (eg.spinosad).
5.	Safer solvents and auxiliaries	Supercritical fluid extraction, synthesis in ionic liquids.
6.	Design for energy efficiency	Polyolefin- polymer alternatives to PWC (polymerization may be carried with lower energy consumption).
7.	Use of renewable feed stocks	Production of surfactants.
8.	Reduce derivatives	On- fiber derivatization vs. derivatization in solution in sample preparations.
9.	Catalysis	Efficient Au (III) - catalyzed synthesis of β -enaminones from 1, 3-dicarbonyl compounds and amines.
10.	Design for degradation	Synthesis of biodegradable polymers.
11.	Real-time analysis for pollution prevention	Use of in-line analyzers for waste water monitoring.
12.	Inherently safer chemistry for accident prevention	Di-Me carbonate (DMC) is an environmentally friendly substitute or di-Me sulfate and Me halides in methylation reactions.

Disposal of chemical waste

Green chemistry is key to reducing waste and improving sustainability. Green chemistry is also finding the safety, improving energy efficiency, and most decisively minimizing or eliminating toxic waste from the beginning. Examples: cfc's (chlorofluorocarbons) in refrigerants, developing the more well-organized way of making pharmaceuticals include—well-known painkiller ibuprofen. With the exception of the many chemical processes found in nature the majority of the chemical process is not completely efficient, require multiple reaction steps and generate hazardous by-products. While in the past traditional waste management focused only on the disposal of toxic by-products and today efforts focused on eliminating waste from the environment by making chemical reaction s more efficient by using biological enzymes, small organic molecules, and metals. Roughly 90 % of industries use catalysts for their industrial process. Solid waste disposal by landfills, oceanic dumping, verification, incineration. Chemical treatment process by neutralization, precipitation, oxidation/reduction, ion exchange, stabilization. A typical chemical process generates products and wastes from raw materials such as substrates, solvents and reagents is shown in figure 6.. If most of the reagents and the solvent can be recycled, the mass flow looks quite different.

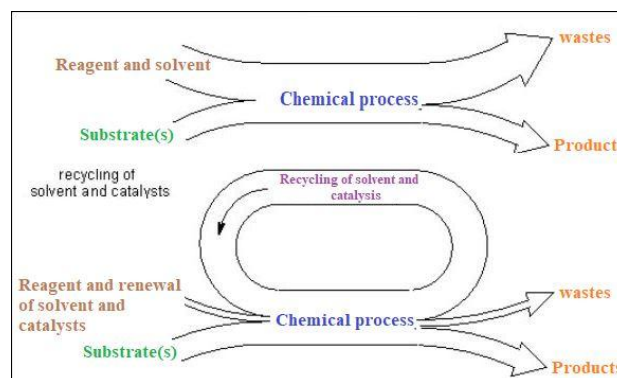


Figure 6: A typical chemical process generates products and wastes from raw materials.

EDUCATION OF GREEN CHEMISTRY⁸

Green chemistry's primary focus is on educating the present day and the future generation chemists, who possess the skill as well as knowledge in order to practice environmentally friendly chemistry. That is why prominent institutes like American Chemical Society and Polish chemical Society are diligently involved in publicizing the rules and attainments of Green chemistry. The ultimate goal is to obtain sustainability by less consumption of natural raw materials and more sensible usage of energy resources, by completely avoiding all states [solid, liquid, gaseous] of fatal wastes, paving a way for more safety products for man. Making Green

chemistry a well-liked topic among every literate person is of paramount importance. Green chemistry holds the key for eco-development. For efficient teaching of green chemistry principles, there are innumerable options, like the Internet and a wide variety of teaching materials. Green chemistry principles and practices are essential to environmentally benign technologies in academia and industry. These activities include:

- ✓ Organizing an interdisciplinary green chemistry workshop on campus.
- ✓ Working with a local company on a green chemistry project.
- ✓ Developing a green chemistry activity with a local school.
- ✓ Converting a current laboratory experiment into a greener one.
- ✓ Organizing a green chemistry poster session on campus.
- ✓ Distributing a green chemistry newsletter to the local community.
- ✓ Designing a green chemistry web page.
- ✓ Increasing awareness among pharmacists and their national organizations.
- ✓ Implementation of environmental policies.
- ✓ Prepare guidelines for pharmaceutical waste management.
- ✓ Working with the government in order to achieve green.
- ✓ The curriculum for green education is included in the syllabus.

CONCLUSION

Green Chemistry is a new approach that through application and extension of the principles of green chemistry can contribute to sustainable development. It is clear that the challenge for the future chemical industry is based on safer products and Processes designed by utilizing new ideas in fundamental research. The success of green chemistry depends on educating the new generation of chemists. For every challenge offered by the green chemistry revolution, there is also an exciting opportunity. Pharmaceutical companies and the Contract

Research and Manufacturing Services (CRAMS) providers have now started employing the principles of green chemistry in developing atom efficient routes, which minimize excess solvents and waste, by utilizing technologies such as a bio or chemo catalysis.

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