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# ORIGINS, CURRENT STATUS AND FUTURE CHALLENGES OF GREEN CHEMISTRY : A REVIEW

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Green Chemistry is the design of chemical products and processes which reduce or eliminates the use and generation of hazardous substance. Over the course of the past decades, Green Chemistry has demonstrated how fundamental scientific methodologies can protect human health and the environment in an economically beneficial manner. Significant progress is being made in several key research areas such as catalysis, the design of safer chemicals and environmentally benign solvent and the development of renewable feedstock. Current and future chemists are being trained to design products and processes with an increased awareness for environmental impact. Outreach activities within the Green Chemistry community highlight the potential for chemistry to solve many of the global environmental challenges as we now face. The origins and basis of Green Chemistry chart a course for achieving environmental and economic prosperity inherent in a sustainable world.

## INTRODUCTION

Green Chemistry address both hazards and those which are associated with global issues like climate change, energy production, availability of a safe and adequate water supply, food preservation and the presence of toxic substances in the environment. Alternative blowing agents replace millions of pounds of chlorofluorocarbons in insulating foams, new energy source lessen our dependence on fossil fuels and pesticides are designed to be more selective and less persistent than traditional organic pesticides. The activities in Green Chemistry research, education, industrial implementation, awards, and outreach are all based on fundamental definition of Green Chemistry.

The concept of "Design" in the definition of Green Chemistry is an essential element in requiring the conscious and deliberative use of a set of criteria, principles and methodologies in the practice of Green Chemistry. The phrase the "use or generation" implies the requirement of life cycle considerations [1]. The term "Hazardous" is used in its broadest context including physical (*e.g.*, explosion, flammability), toxicological (*e.g.*, carcinogenic) and global (*e.g.*, Ozone depletion, climate change).The design of environmentally benign products and processes may be guided by the twelve principles of Green Chemistry. The challenge of sustainability will be met with new technologies that provide society with the products we depend on in an environmentally responsible manner. The twelve principle of Green Chemistry [2] are:

1. **Prevention :** It is better to prevent waste than to treat or clean up waste after it has been created.

2. **Atom Economy :** Synthetic methods should be designed to maximize the incorporation of all materials used in the process in to the final product.
3. **Less Hazardous Chemical Syntheses :** Whenever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals :** Chemical products should be designed to effect their desired function while minimizing toxicity.
5. **Safer Solvents and Auxiliaries :** The use of auxiliaries' substances (e.g., Solvents, separation agents etc) should be made unnecessary wherever possible and innocuous when used.
6. **Design for Energy Efficiency :** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstocks :** A raw material or feedstocks should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce Derivatives :** Unnecessary derivatization should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. **Catalysis :** Catalytic reagents (as selective as possible ) are superior to stoichiometric reagents.
10. **Design for Degradation :** Chemical products should be designed so that at the end of their function they break down in to innocuous degradation and do not persist in the environment.
11. **Real Time Analysis for Pollution Prevention :** Analytical methodologies need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention :** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.

## History

The term Green Chemistry was first used in 1991 by P.T. Anastas in a special program launched by the US environmental protection agency (EPA) to implement sustainable development in chemistry and chemical technology by industry, academia and government. In 1995 the annual US Presidential Green Chemistry Challenge award was announced. Similar awards were soon established in European countries. In 1996 the working party on Green Chemistry was created, acting within the frame work of International Union of Pure and Applied Chemistry. One year later, the Green Chemistry Institute (GCI) was formed with chapter in 20 countries facilitate contact between governmental agency and industrial corporations with universities and research institutes to design and implement new technologies. The first conference highlighting Green Chemistry was held in Washington in 1997.Since that time other similar scientific conferences have soon held on a regular basis. The first book and journals on the subject of Green Chemistry were introduced in 1990s, including Journal of Clean Processes and Products and Green Chemistry, sponsored by Royal Society of Chemistry. Other journals such as Environmental Science and Technology and the Journal of Chemical education, have devoted sections to Green Chemistry.

# CURRENT STATUS OF GREEN CHEMISTRY

In some industrial chemical processes, not only waste products but also the reagents used for the production may cause a threat to the environment. The risk of exposure to hazardous chemical compounds is limited in daily work by protective equipment such as goggles, breathing apparatus, face-guard masks, etc. According to the principles of Green Chemistry, a threat can be eliminated in a simpler way, by applying safe raw materials for production process.

Large amounts of adipic acid [HOOC $(CH_2)_4$ COOH] are used each year for the production of nylon, polyurethanes, lubricants and plasticizers. Benzene-a compound with convinced carcinogenic properties- is a standard substrate for the production of this acid. Chemists from State University of Michigan developed green synthesis of adipic acid using a less toxic substrate. Furthermore, the natural source of this raw material-glucose – is almost inexhaustible. The glucose can be converted into adipic acid by an enzyme discovered in genetically modificated bacteria [3]. Such a manner of production of this acid guards the workers and the environment from exposure to hazardous chemical compounds.

Green Chemistry tries, when possible, to utilize benign, renewable feedstocks as raw materials. From the point view of Green Chemistry, Combustion of fuels obtained from renewable feedstock is more preferable than combustion of fossil fuels from depleting finite sources. For example, many vehicles around the world are fueled with diesel oil, and the production of biodiesel oil is promising possibility. As the name indicates, biodiesel oil is produced form cultivated plants oil, e.g. from soya beans.

Biodiesel oil also can be obtained from wasted plant oils e.g. oils used in restaurants. In the technological process, a potential waste product is transformed into valuable fuel (Combusted biodiesel oil smells like fried potatoes).The advantages of using biodiesel oil are obvious. It’s fuel from renewable resources and contrary to normal diesel oil, the combustion of biodiesel does not generate sulphur compounds and generally does not increase the amount of carbon dioxide in the atmosphere. $CO_2$ formed in the combustion of fuel was removed earlier by plants [3].

The great threats to the environment are organic solvents applied in many syntheses. They are released into the environment by a volatilization process, especially in the case of volatile organic compounds (VOCs) and as a result of leakage. The emission of such compounds is significant because in many syntheses their amount exceeds the amount of reagents. The new solutions for practical synthesis aim at complete elimination of solvents or to substitute the compounds, belonging to VOCs by cheap technological media, harmless for humans and the environment.

The use of supercritical fluids (SCFs) in chemical processes is becoming more and more prevalent [4-8]. The term “supercritical fluids” comprises the liquids and gases at temperatures and pressure higher than their critical temperature and pressure. Above the critical point the liquid-vapour phase boundary disappears while the formed phase exhibits properties between those of gas and liquid. High compressibility of supercritical fluids in the vicinity of the critical point makes it easy to adjust density and solution ability by a small change of temperature or pressure. Due to this, the supercritical fluids are able to dissolve many compounds with different polarity and molecular mass. Among many possible supercritical fluids, fulfilling the Green Chemistry demands as the reaction media are carbon dioxide ($scCO_2$) and water ($scH_2O$).

Carbon dioxide as a supercritical fluid is most frequently used as medium for reactions. It is inflammable, easily available (from natural sources, from power engineering) and cheap. It's application given considerable energy savings because the critical point is easy to reach due to a low evaporation heat of $CO_2$. Carbon dioxide as a supercritical fluid dissolves non-polar compounds and come polar (e.g. methanol, acetone) like fluorocarbon solvents. The discovery of a new surfactant with high surface activity in supercritical carbon dioxide opened a way to new process in textile and metal industries and for dry cleaning of clothes. Micelle Technologies Company offers technology for removal of stains using liquid carbon dioxide instead of the perchloroethylene more commonly applied [9].

Most of the common liquids (e.g., water, ethanol, benzene, etc) are molecular. That is, regardless of whether they are polar on non-polar, they are basically made up of molecules. However, since the early 1980s an exciting new class of room-temperature liquids have become available. These are the ambient-temperature ionic liquids. Unlike the molecular liquids, regardless of the degree of association, they are basically constituted of ions. This gives them the potential to behave very differently from conventional molecular liquids when they are used as solvents.

Room-temperature ionic liquids are considered to be environmentally benign reaction media because they are low-viscosity liquids with no measurable vapour pressure. However, the lack of sustainable techniques for the removal of products from the room-temperature ionic liquids has limited their application. Professors Brennecke and Beckman have shown that environmentally benign carbon dioxide, which has been used extensively, both commercially and in research for the extraction of heavy organic solutes, can be used to extract non volatile organic compounds from room temperature ionic liquids [10]. They found that extraction of a material into carbon dioxide represents an attractive means for recovery of products from ionic liquids because:

(a) $CO_2$ dissolves in the ionic liquid to facilitate extraction and

(b) the ionic liquid does not dissolve appreciably in the $CO_2$,

So that product can be recovered in pure form. The research groups of Professors Brennecke and Beckman have shown that ionic liquids (using 1-butyl-3-menthylimidazolium hexa fluorophosphate as a prototype) and $CO_2$ exhibit extremely unusual, and very attractive, phase behaviour. The solubility of $CO_2$ in ionic liquids is substantial, reaching mole fractions as high as 0.6 at just 8 MPa. Yet the two phases do not become completely miscible, so $CO_2$ can be used to extract compounds from the ionic liquids. Most importantly, the composition of the $CO_2$- rich phase is essentially pure $CO_2$ and there is no measurable cross contamination of the $CO_2$ by the ionic liquid. Moreover, non-volatile organic solutes (using naphthalene as a prototype) may be quantitatively extracted from the ionic liquid with $CO_2$, demonstrating the tremendous potential of ionic liquid/$CO_2$ biphasic systems as environmentally benign solvents for combined reaction and separation schemes.

## Future Challenges

The future challenges facing Green Chemistry are as diverse as the scientific imagination and address the broadest issues of sustainability. Because of this breadth, it should be no surprise that a number of these challenges are being pursued for reasons ranging from economic to scientific.

## Research Challenges

The challenges to research in achieving Green Chemistry principles are numerous, and a detailed discussion of each is not possible. However, a listing of some of the challenges provides an illustration of current issues and may stimulate thinking on other challenges that should be included:

- Transformation utilizing energy rather than material.
- Efficient splitting of water by visible light.
- Solvent systems that effect efficient heat and mass transfer while catalyzing reactions and intrinsically aiding in product separation.
- Development of a synthetic methodologies " toolbox" that is both atom economical and benign to human health and the environment.
- Plastics and polymers designed for innocuous degradation through the use of additives free design.
- Materials design for recycle/reuse decisions based on embedded entropy.
- Development of "Preventative toxicology" where increasing knowledge of biological and environmental mechanisms of action are continuously incorporated into the design of chemical products.
- Less energy intensive manufacture of photovoltaic cells that are more efficient.
- Development of no combustion, non-material-intensive energy sources.
- Value added consumptive/fixation uses for $CO_2$ and other greenhouse gases at high volume.
- Transformations preserving sensitive functionality without the use of protecting group.
- Development of surfaces and materials that are durable and do not require coatings and cleaners.

**Implementation Challenges.** The discovery of more environmentally benign technologies at the research stage does not guarantee that they will be adopted on an industrial scale. A number of barriers hinder the adoption of newer technologies that prevent pollution. Adoption of environmentally benign processes may be facilitated by the following:

- Flexibility in regulations.
- Tax incentives for implementing cleaner technologies.
- Research programs to facilitate technology transfer among academic institutions, government, and industry.
- Patent life extensions for cleaner process optimization.

## Education Challenges

Students at all levels can be introduced to the philosophy and practice of Green Chemistry. Educators need appropriate tools, training and materials to effectively integrate Green Chemistry into their teaching and research. Important steps to be taken to advance Green Chemistry within the curriculum include the following:

- Systematic recognition of hazard/toxicity as a physical/chemical property of molecular Structure, that can be designed and manipulated.

- Development and utilization of practical laboratory experiments to illustrate green Chemistry principles.
- Balanced equations in organic textbooks and replacement of “yield” with “atom economy”.
- Introduction of the basic concepts of chemical toxicology and the molecular basis of hazard.
- Incorporation of Green Chemistry topics on professional certification exams.
- Teacher reference materials for incorporating Green Chemistry into existing courses.
- Education of legislators on the benefits of Green Chemistry.

## CONCLUSION

The growth of Green Chemistry over the course of the past decade needs to increase at an accelerated pace if molecular science is to meet the challenges of sustainability. It has been said that the revolution of one day becomes the new orthodoxy of the next. When the 12 Principles of Green Chemistry are simply incorporated as an integral part of everyday chemistry, there will no longer be a need for the focusing, highlighting, and moniker of Green Chemistry and when that day comes, the challenges that chemistry will meet cannot be imagined.

## REFERENCES

1. Anastas, P.T., Lankey R.L., Life Cycle Assessment and Green Chemistry, *The Yin and Yang of Industrial Ecology. Green Chemistry,* 289 (2000).
2. Anastas P.T, Warner J.C., Green Chemistry: Theory and Practice, *Oxford University Press: New York,* 30 (1998).
3. Merrill, M., Parent, K., Kirchhoff, M., Green Chemistry: Stopping Pollution Before it Starts, *Chem. Matters,* 7 (2003).
4. Jessop, P.G., Leitner, W., *Chemical Synthesis using Supercritical Fluids*, Wiley-VCH Weinheim, (1999).
5. Sarrade, S., Guizard, C., Rios, G.M., New Applications of Supercritical Fluids and Supercritical Fluids Process in Separation, *Separation and Purification Technology*, **32**, 57 (2003).
6. Brannegand, D.R., Ashraf-Khorassani, M., Taylor, T.L., Supercritical Fluids Extraction of Ethoxyquin from a Beef Matrix, *Chromatographia,* **54**, 399 (2001).
7. Wolski, T., Ludwiczuk, A., Extraction of Natural Products with Supercritical Gases, *Prezem. Chem*., **80**, 286 (2001).
8. Skowronski, B., Mordecka, Z., Polish Insallation for Supercritical Extraction of Hops, *Przem. Chem.,* **80**, 521 (2001).
9. http://www.micell.com
10. The Presidential Green Chemistry Challenge Awards Program. Summary of 2000 Award Entries and Recipients,www.epa.gov/greenchemistry (2001).

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