

Impact of Green Chemistry In Present Scenario

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Abstract

Chemists have used their knowledge and skill to prepare a large number of new materials which are far better and more useful than the natural products, such as high-tech polymers, liquid crystals, tough ceramics, nonlinear optical substances, novel electronics, designer drugs, genetic materials and new energy sources. The term *Green Chemistry* was coined in 1991 by Anastas. The purpose is to design chemicals and chemical processes that will be less harmful to human health and environment. Green chemistry protects the environment, not by cleaning up, but by inventing new chemical processes that do not pollute. Green chemistry seeks to reduce pollution at source, whereas environmental chemistry focuses on the study of pollutant chemicals and their effect on nature. *Designing Safer Chemicals*: New products can be designed that are inherently safer for the target application. *Safer Solvents and Auxiliaries*: Solvents are extensively used in most of the syntheses. *Use of Renewable Feedstocks* Chemical transformations should be designed to utilize raw materials and feedstocks that are renewable, but technically and economically practicable. *Use of Catalyst*: Catalysts are used in small amounts and can carry out a single reaction many times and so are preferable to stoichiometric reagents, which are used in excess and work only once. They can enhance the selectivity of a reaction, reduce the temperature of a transformation, reduce reagent-based waste and potentially avoid unwanted side reactions leading to a clean technology. The values and positive impact of green chemistry to tomorrow's in different fields.

Key words: Green chemistry, green syntheses, green solvents,

Introduction

Green chemistry is a highly effective approach to pollution prevention because it

applies innovative scientific solutions to real-world environmental situations. The Pollution Prevention Act of 1990 established a national policy to prevent or reduce pollution at its

source whenever feasible. The Pollution Prevention Act also provided an opportunity to expand beyond traditional EPA programs and devise creative strategies to protect human health and the environment. Green chemistry is the use of chemistry for pollution prevention. More specifically, green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Promoting this new approach to pollution prevention through the environmentally conscious design of chemical products and processes is the focus of EPA's Green Chemistry Program.

GREEN CHEMISTRY[™] was coined by Professor Paul Anastas, who is known as the father of green chemistry, at US Environmental Protection Agency. Green Chemistry is the effort of reducing or eliminating the use of or generation of hazardous substances in the design, manufacture and application of chemical products.¹ Green Chemistry has changed our life style in many ways. Like now a days dry cleaning of clothes is done with the use of liquid CO₂ and a surfactant, thereby eliminating a need of halogenated solvents like PERC (perchloroethylene Cl₂C=CCl₂).² This technology is known as micell Technology. In the same way, hydrogen peroxide (H₂O₂) is used with some activators like TAML³ activators as a bleaching agents rather than the use of halogenated compounds. Green Chemistry has been referred by a number of alternate name like "Clean Chemistry", 'Atom Economy', Brought by Design Chemistry¹ 'sustainable chemistry'⁴, 'Eco-friendly chemistry' and 'Environmentally Benign Chemistry'.

Green Chemistry Is About...

Source Reduction/Prevention of Chemical Hazards

Design chemical products to be less hazardous to human health and the environment

Use feedstocks and reagents that are less hazardous to human health and the environment

Design syntheses and other processes to be less energy and materials intensive (high atom economy, low E-factor)

Use feedstocks derived from annually renewable resources or from abundant waste

Design chemical products for increased, more facile reuse or recycling

Reuse or Recycle Chemicals

Treat Chemicals to Render Them Less Hazardous

Dispose of Chemicals Properly

Chemicals that are less hazardous to human health and the environment are:

Less toxic to organisms and ecosystems

Not persistent or bioaccumulative in organisms or the environment

Inherently safer with respect to handling and use

Twelve Principles of Green Chemistry :

1. Prevent waste:

Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.

2. Design safer chemicals and products:

Design chemical products to be fully effective, yet have little or no toxicity.

3. Design less hazardous chemical syntheses:

Design syntheses to use and generate substances with little or no toxicity to

humans and the environment.

4. Use renewable feedstocks:

Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.

5. Use catalysts, not stoichiometric reagents:

Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.

6. Avoid chemical derivatives:

Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

7. Maximize 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.

8. Use safer solvents and reaction conditions:

Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.

9. Increase energy efficiency:

Run chemical reactions at ambient temperature and pressure whenever possible.

10. Design chemicals and products to degrade after use:

Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

11. Analyze in real time to prevent pollution:

Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

12. Minimize the potential for accidents:

Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

SOME WELL-PUBLICIZED INCIDENTS FROM THE PAST FEW DECADES...

- The Cuyahoga River in Ohio became so polluted with chemicals it caught fire.
- A plant accident in Bhopal, India, released methyl isocyanate. Nearly 4000 people died.
- An accidental release of chemicals, including dioxin, in Seveso, Italy, in 1976 resulted in death of farm animals and long-term health problems for many local residents.

MANY COUNTRIES HAVE ALREADY ENACTED LAWS AND SIGNED INTERNATIONAL TREATIES TO REDUCE POLLUTION LEVELS, INCLUDING:

- Montreal Protocol to Protect the Ozone Layer
- Global Treaty on Persistent Organic Pollutants
- Rio Declaration on Environment and Development

Examples of Green Chemistry :

- New syntheses of Ibuprofen and Zolofit.
- Integrated circuit production.
- Removing Arsenic and Chromate from pressure treated wood.
- Many new pesticides.
- New oxidants for bleaching paper and disinfecting water.
- Getting the lead out of automobile paints.
- Recyclable carpeting.
- Replacing VOCs and chlorinated solvents.
- Biodegradable polymers from renewable resources.
- Safer dry cleaning
- Initially gasoline and kerosene were used
- Chlorinated solvents are now used, such as perc
- Supercritical/liquid carbon dioxide (CO₂)

LEAD POLLUTION HAS BEEN DECREASED BY...

- Replacing lead in paint with safe alternatives, and
- Replacing tetraethyl lead with less toxic additives (e.g., "lead-free" gasoline).

CHEMICAL FOAMS TO FIGHT FIRES.

- Millions of tons of chemical fire-fighting foams used worldwide have discharged toxic substances into the environment,

contaminating water supplies and depleting the ozone layer.

PUTTING OUT FIRES THE GREEN WAY..

- A new foam called Pyrocool FEF has now been invented to put out fires effectively without producing the toxic substances found in other fire-fighting materials.

CHEMICALS FOR DRY CLEANING..

- Perchloroethylene ("perc") is the solvent most widely used in dry cleaning clothing.
- Perc is suspected of causing cancer and its disposal can contaminate ground water.

USE CATALYSTS

- Catalyst is a reagent which enhance the rate of a chemical transformation but is not consumed during the reaction.
- Since the rate is enhanced, lower reaction temperature can be used and thus can save energy.
- Some catalysts can improve the selectivity of a reaction, thus giving higher yield of the desired product. This can reduce waste.
- A catalytic reaction is in general superior to a reaction requiring stoichiometric reagents in terms of reducing waste.

Biocatalysis⁵, in contrast involves aqueous environments. Reduction of aldehydes or ketones to alcohols using bio-catalyst.⁶ The range of reactions that can be carried out with whole cells is enormous, given the range of microorganisms that have already been isolated or remain to be discovered. Microbial cells can

be employed as very effective reactors for the conversion of substrates to products, operating in mixed aqueous – a polar systems. Optimized for the best space time yields attainable at lowest costs. Biodegradation of toxic pollutants in the wastewater treatment technologies, by using microbes is well known. Just as light, heat and moisture can degrade many materials, biotechnology relies on naturally occurring, living bacteria to perform a similar function. Some bacteria naturally “feed” on chemicals and other wastes including some hazardous materials. They consume those materials, digest them, and excrete harmless substances in their place. According to William K. Reilly, former head of the Environmental Protection Agency, “The use of biotechnology to solve environmental problems, could be - should be - an environmental breakthrough of staggering positive dimensions”.

Solvent-free organic syntheses^{7,8}

In general, easier for unimolecular reactions; not easy for reactions involving two or more reactants; not easy for reactants which are solid at reaction temperature; not easy for reactions involving heating as heat exchange is difficult; *microwave heating!*

General principles of microwave :

Microwave region of the electromagnetic spectrum: 1 cm to 1 m; Most domestic microwave operate at 2.45 GHz; Microwave radiation is generated by a magnetron, the microwaves are guided into the cavity by a waveguide and reflected by the walls of the cavity; variable power levels to 1100 Watts. When a molecule is irradiated with microwaves,

it rotates to align itself with the applied field; Qualitatively, the larger the dielectric constant of a substance, the greater the coupling with microwave, and thus the greater heating; That is: polar compounds, water, methanol, dimethylformamide, etc. are heated when irradiated with microwave; Non-polar compounds, hexane, toluene, ethers, carbon tetrachloride, etc. do not heat with microwave irradiation.

Solvent-free reactions: conventional heating versus microwave :

- For reactions involving liquids:
 - If the reagents are polar, the mixture can be heated with microwave and rotated for short intervals;
 - Some time cooling is necessary to moderate the reactions for fear of runaway reactions (explosion). Microwave assisted reaction with water moderation⁹
- Avoid/ minimize chemical derivatives*
- In a chemical synthesis, the use of blocking groups (derivatives) or protecting/ deprotection should be avoided or minimized because such steps require additional reagents and generate waste.
 - That means more selective chemical reactions or reagents need to be developed and deployed. Example: reaction of α hydroxy-aldehyde with organometallic reagents¹⁰
 - The protection-deprotection sequence adds two more steps, and requires additional reagents, solvents, etc.
 - A more selective reaction is required: a reagent which selectively reacts with the aldehyde function, but not with the hydroxyl function.

Ultrasonic synthesis gives excellent yield compared to other reactions. The use of

microwave energy¹¹ instead of conventional heating, often results in good yields in very short time. Lewis¹² stated enhancement of a chemical reaction in microwave as compared to conventional heating. A recent survey shows that more than a thousand publications have appeared on microwave mediated chemical reactions¹³. In microwave, 2,3-Dimethyl indole was obtained with 67% yield from phenylhydrazine and butane-2-one at 220°C for 30 min.¹⁴

Concept of atom economy :

- First proposed by Prof. Barry M. Trost^{15,16} of Stanford University in 1991. It is a measure of the inherent efficiency of a chemical reaction.

- Percent atom economy of a reaction = $\frac{\text{molecular weight of desired product}}{\text{molecular weight of all products (or reactants)}} \times 100$. Example preparation of propylene oxide from propene by the chlorohydrin route, a current industrial process.

Mass Intensity and Reaction Mass Efficiency¹⁷

Reaction Mass Efficiency:

Mass of isolated product X 100%

Total mass of reactants used

Mass Intensity:

Total mass for reaction (reactants, solvents, auxiliaries)

Mass of product

Environmental impact of a chemical reaction:

- In research development, search for new

reactions which are atom economical,

- Improve the yield, thus improve the reaction mass efficiency,

- Equally important is to reduce mass intensity through reduction of solvents; acids or base for neutralization; or other substances required for reaction.

Use safer solvents and auxiliaries :

- Solvents are used as reaction media, in separation/purification and in cleaning technologies;

- Many common organic solvents (e. g. hexane, chloroform, ether, ...) are volatile and contribute to environmental pollution as volatile organic compounds (VOC);

- Some common organic solvents are toxic: benzene is known to cause leukemia; excessive exposure to n-hexane causes neurotoxicity.

- The use of auxiliary substances (e. g. solvents, separation agents, drying agents.) should be reduced or made unnecessary where possible, and innocuous when used.

Liquid or supercritical carbon dioxide as reaction media or extraction solvent. Supercritical carbon dioxide (SC-CO₂)¹⁸⁻²¹ is an attractive alternative because it is inexpensive and poses no threat to the environmental or human health²².

- A supercritical fluid (SCF) is the defined state of a compound, mixture or element above its critical pressure (P_c) and critical temperature (T_c) but below the pressure required to condense it into a solid.

	T_c (oC)	P_c (bar)
CO ₂	31.1	73.8

Chemical Synthesis Using Liquid or Supercritical Carbon Dioxide.

- Liquid or SC-CO₂ as an alternative “green” solvent—non-toxic, non-flammable, inexpensive, environmentally benign;
- Basic Physical Properties:
 - solvating power similar to hexane and CCl₄;
 - Miscibility with gases such as H₂ and O₂;
 - Can evaporate as gas on lowering to atmospheric pressure, therefore facilitates purification. Useful for extraction (decaffeinated coffee). Extraction of limonene from orange peel with liquid carbon dioxide²³.

Conclusions

Green Chemistry for The Present and Future Scenario :

- *Research*: intellectually more challenging by imposing new constraints of use of reagents, solvents, and reaction conditions.
- *Practice*: will be implemented if the “green” process is more economical. This means additional research challenge in meeting the twin goals of “atom economy” as well as real economy.
- *Education*: in the chemistry curriculum and, more broadly, science education, the ideas of “green chemistry” must be incorporated.

The values of green chemistry to tomorrow's chemists. They should learn to assess hazard with this knowledge and to adopt more sustainable chemical practices throughout their academic and industrial career.

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