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Enzymes in green chemistry: The need for environment and sustainability

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Abstract
Green chemistry is rapidly emerging area of chemical research today which is associated with research and applications of chemical processes which are environmental benign, economical and less polluting. Green chemistry is based on certain principles emphasising on the reduction or elimination the use and generation of hazardous substances in all steps of chemical synthesis or process. Chemists and scientists are working to minimizing the risk for human health and the environment by following all the valuable principles of green chemistry. The green chemistry insists to utilize eco-friendly, non-hazardous, reproducible and efficient solvents and catalysts and chemicals in synthesis of various molecules and in researches. Enzymes are important tools in green chemistry as they act as catalysts which accelerate the chemical reactions, works without using harsh conditions and chemicals and are reusable.

Keywords: Green Chemistry, Environment, Enzymes, Chemical synthesis

1. Introduction
Green chemistry is a relatively new area of chemistry that aims to the need of reducing the hazardous effect as well as the amount of chemicals towards environmental pollution. Green Chemistry is defined as development and application of chemical products and processes tend to reducing or eliminating the use and generation of hazardous substances for human health and environment. Green chemistry also includes invention and design of processes in the direction of development and application of efficient chemical processes and products. Today the green chemistry revolution is providing enormous challenges for chemists and researchers in industry, education or research sector. These challenges are opening the doors of new opportunities to discover and apply new methods in synthetic chemistry. Green chemistry is concerned with the study about designing the process or products that will not involve materials harmful to the environment.

2. Green Chemistry
During the last century, chemistry has changed human lifestyle with emergence in almost every aspect of life and our everyday needs- starting with toothpaste (colloids), breakfast and food (proteins, carbohydrates), hair oil, bathing and washing clothes (soaps, washing powder), cleaning the home (cleansing agents, phenyl), transport (petrol, diesel, LPG), dietary supplement (proteins, vitamins, minerals) and medicines, all are chemicals.
Chemical industry has increasing everyday consistently. Chemical industry consists the production and use of chemicals, reagents, solvents, catalysts and almost all type of organic reactions for synthesizing a variety of compounds and molecules. Many chemicals and chemical processes are very hazardous, toxic and have adverse effects on the environment as well as human health. Synthetic, Pharmaceuticals and fine chemicals Industries produce relatively more waste, which is harmful for environment and nature.
During the early 1990s the US Environmental Protection Agency (EPA) coined the term Green Chemistry to promote innovative chemical technologies that are associated with reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products.

Green chemistry process is designed to reduce or eliminate negative environmental impacts like the usage and production of chemicals involving reduced waste products, non-toxic components, and improved efficiency. It is chemistry that deals with the application of environmentally friendly chemical compounds in the various areas of our life including industrial uses and other areas. Green chemistry has an emphasis on the design of chemical products and processes. This approach tries to offer environmentally beneficial alternatives to more hazardous chemicals and processes, and thus promotes pollution prevention.

Green chemistry efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products.

2.1 History of Green Chemistry

In 1990 the Pollution Prevention Act was passed in the United States. This act helped create a work plan for dealing with pollution in an original and innovative manner. This paved the way to the concept of green chemistry. Paul Anastas and Warner coined the word "green chemistry" and developed the twelve principles**.** Ryoji Noyori identified three key developments in green chemistry: use of supercritical carbon dioxide as green solvent, aqueous hydrogen peroxide for clean oxidations and the use of hydrogen in asymmetric synthesis.

Green chemistry had been developed by the need to avoid chemical hazards that organic and inorganic compounds produce on the livings. Since its origin there has been a remarkable progress in this area of science.

2.2 Concept of Green Chemistry

The concept of green chemistry includes a new approach towards the synthesis, processing and application of chemical substances in such a manner which reduce threats for environment and health. This new approach is also called as clean chemistry or environmentally benign chemistry. Green Chemistry is the designing of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.

For example in green chemistry we can use water as the medium of chemical reactions in the laboratory avoiding pollution and the hazardous effect of the volatile solvent. Green chemistry applies combined approaches of organic chemistry, inorganic chemistry, biochemistry, analytical chemistry and physical chemistry to minimize waste and utilize renewable resources.

Green Chemistry has been considered as an important area of scientific research and The Nobel Prize Committee recognized the importance of green chemistry in 2005 by awarding Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock the Nobel Prize for Chemistry for "the development of the metathesis method in organic synthesis."

3. Principles of Green Chemistry

Green chemistry is a highly effective approach to prevention of environment pollution as for energy conservation as it applies innovative scientific approaches to solve real-world environmental situations. Green chemistry is based on certain principles which are called as 12 principles of Green Chemistry. These 12 principles of Green Chemistry provide a way to implement the strategies of green chemistry action plan which are listed below-

- Prevention It is better to prevent waste than to treat or clean up waste after it has been created.
- Atom Economy Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- Less Hazardous Chemical Syntheses Synthetic methods should be designed, wherever practicable, to use and generate substances that possess little or no toxicity to human health and the environment.
- Designing Safer Chemicals Chemical products should be designed to achieve their desired function while minimizing their toxicity.
- Safer Solvents and Auxiliaries Unnecessary use of auxiliary substances (e.g., solvents, separation agents, etc.) should be avoided wherever possible and made innocuous when used.
- 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.
- Use of Renewable Feedstocks Whenever technically and economically practicable, raw material or feedstock should be renewable rather than depleting it.
- Reduce Derivatives Unnecessary derivatization (use of blocking groups, protection or deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- Catalysis Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- Design for Degradation Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
- 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.
- Inherently Safer Chemistry for Accident Prevention Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential of chemical accidents, including releases, explosions, and fires.

The greenness of a chemical transformation is generally assessed on the context of its safer application and practice in life. For proper implementation of green chemistry in practice all these principles must be well considered and followed.

4. Enzymes in Green Chemistry

Enzymes are biological catalysts existing in living systems. Chemically these are made from proteins and perform very specific biochemical tasks. Enzymes have emerged as preferred tools in green chemistry and increasingly used in industrial processes due to their ability to catalyze reactions with high catalytic efficiency and specificity. Enzymes have found their application in many environment friendly industrial and chemical processes today. Enzymes have applications in several aspects of our life, such as in detergents, leather, paper and pulp, textile, cosmetic, healthcare and pharmaceutical and food processing industries, for clinical and diagnostics research and also for organic synthesis in non-aqueous media. Enzymes are increasingly used in industrial processes also due to their ability to catalyze reactions with high catalytic efficiency and specificity. Enzymes based reactions are replacing hazardous processes

and toxic chemicals / by-products and are powerful and important part of industrial sustainable chemistry e.g. in production of herbicides and chiral drug intermediates.

Today a Google search for 'enzymes in green chemistry' produces 20,00,000 results in 0.37 seconds showing their importance.

The world market for enzyme production and application in chemical sector is growing bigger every day, and the demand for useful biocatalysts is increasing rapidly. The report **"**Industrial Enzymes Market" has predictions that the industrial enzymes market will grow worth 6.2 Billion USD by 2020. The increase in the number of applications of industrial enzymes, investments in the research & developments of industrial enzymes and the need of cost reduction and resource optimization in the production process are driving factors for the growth of global industrial enzymes market. The key players in the global enzyme market are BASF SE (Germany), E.I. du Pont de Nemours and Company (U.S.), Associated British Foods plc (U.K.), Koninklijke DSM N.V (The Netherlands), and Novozymes A/S (Germany) among others. The industrial enzymes market was valued at USD 4.2 Billion in 2014 and is projected to grow at a CAGR (compound annual growth rate) of 7.0% from 2015 to 2020. In 2014, the market was dominated by North America. At present the Asia-Pacific region is projected to grow at the highest CAGR from 2015 to 2020.

4.1 Benefits of using enzymes in Chemical synthesis-

Enzymes offer following advantages over other chemical catalysts-

- Enzymes operate under milder conditions.
- Enzymes offer high optical purity.
- Enzymes offer high chemo selectivity, high region- and stereo-selectivity.
- Enzymes are alternative for polluting and harsh chemicals.
- These involve lesser use of hazardous and harsh chemicals as intermediates.
- Enzymatic reactions are easy to control.
- Enzymes produce no harmful by-products.
- Enzymes are biodegradable and reusable.

4.2 Some Examples of Enzymes in Chemical synthesis

Enzymatic catalysis is being seen as a promising option in the area of chemical synthesis.

Enzyme based processes are today being widely applied for the production of different chemicals. Some of the examples of usage of enzymes in green chemical processes are given below-

- Lipases are used for the production of enantiopure alcohols and amides, nitrilases for the production of enantiopure carboxylic acids, and acylases for the production of new semisynthetic penicillins.
- Acylase are used for synthesis of semisynthetic penicillin, the use of Nitrilase for Synthesis of enantiopure carboxylic acids.
- Enzyme Laccase and manganese peroxidise catalyzes oxidation of phenols.
- In oxidative biotransformation reactions– monooxygenases are used for biotransformation of Ketones to esters or lactones, in Baeyer–Villiger oxiation, in biotransformation of Terminal alkenes to (R)-epoxides, and Substituted phenols to hydroxybenzaldehydes.
- Steroid hydroxylases catalyze the site specific hydroxylation of steroids and many other terpenoid, benzylic or alicyclic compounds.
- Chloroperoxidase are used in the oxidation of S-alkylcysteine derivatives to yield sulfoxides.
- The application of lipases in synthetic biotransformations in non aqueous media consists a wide range of solvolytic reactions of the carboxyl group, like esterification, transesterification (alcoholysis), perhydrolysis and aminolysis (amide synthesis).
- Subtilisin, an endoprotease, is used in the enantioselective hydrolysis of N-acylamino acid esters into the corresponding (S)-amino acids.
- Glycosidases hydrolyse glycosidic bonds but they are also widely used as biocatalysts for carbohydrate synthesis *in vitro*, such as in the transglycosylation of lactose with N-acetylglucosamine.
- In Reduction of carbonyl groups such as aldehydes and ketones - Alcohol dehydrogenases (ADH) are the preferred catalysts for these reduction reactions with ketoreductases (KRED), carbonyl reductases (CR), which are frequently used. These are generally termed as dehydrogenase (DH) and are useful in-

a. Amino acid dehydrogenases (AaDHs) perform the reductive amination of a-ketoacids
b. In Reduction of acids tungsten containing aldehyde oxidoreductases (AOR) first reduce the aldehyde, which is followed by an ADH-catalysed further reduction to the alcohol.
c. For the enantiospecific reduction of conjugated C Cdouble bonds, the enoate reductases are applied.

5. Green Chemistry and Sustainable Development

The UN defines sustainable development as 'meeting the needs of present without compromising the ability of future generation.' Green chemistry focuses on how to achieve sustainability through science and technology. This is possible by-

- Better understanding and solving the issue of environmental pollution, many approaches and models have been developed for environmental impact assessments.
- Some of these approaches and models have been successful in predicting impacts for selected chemicals in selected environmental settings.
- These models have joined air and water quality aspects to point and nonpoint sources and have been very useful for the development of emission control and compliance strategies.
- However, some of the approaches and models were aimed primarily at evaluating the quantity of pollutants that could be discharged into the environment with acceptable impact, but failed to focus on pollution prevention.
- The concept of waste management, and strategies such as environmentally conscious manufacturing, eco efficient production or pollution prevention gained recognition are useful tools to achieve sustainability.

6. Recent Trends in Green Chemistry

Chemists are practicing green chemistry thinking about reoptimization timeframes, costs, access to established chemicals, and also the methods and regulatory issues. The goal is to identify the most environmentally benign conditions

for chemical transformations and analyze reactions for five green criteria:

1. the environmental degradation of reagent and degradation products,
2. solvent compatibility to green solvents, and availability from natural feedstock,
3. atom efficiency of transformation,
4. Toxicity and process safety hazards.

Today Many innovative companies are practicing green chemistry, citing environmental sustainability, increased efficiency, and lowered costs, as they develop the tools and measurements that inform the choices of solvents and reagents throughout a compound's development and manufacturing.

At the American Chemical Society's (ACS) recent "Green Chemistry and Engineering" conference, Richard Williams, president and founder of Environmental Science & Green Chemistry Consulting, said "Green chemistry is gaining prominence, paralleling regulatory and economic movements. There is a global expectation for sustainable resource use, chemical safety, and transparency as stakeholders are becoming more precautionary and risk adverse." He also stated "Green chemistry is just good chemistry, as new science develops, it delivers economic and environmental benefits."

Some of the current practices in the direction are listed below-

- Pfizer improved the manufacturing process for sertraline, the active ingredient in Zoloft®." The original three step sequence was reduced to one step, producing chirally pure sertraline in much higher yield and with greater selectively and decreased Raw material usage.
- Employing ethanol as a solvent eliminated the use, distillation, and recovery of four more hazardous solvents. The green approach has eliminated nearly 2 million pounds of chemical waste per year, improved safety and material handling, reduced energy and water use, and doubled overall product yield.
- Immediate challenges include reducing chlorinated solvent usage, phasing out toxic and non-economical reagents, modifying wasteful ordering and disposal habits, and encouraging use of green conditions.
- Other effective measures include- replacing dichloromethane chromatography with greener solvent systems (like heptanes, ethyl acetate, and ethanol) and by replacing normal-phase chromatography with reverse phase medium pressure liquid chromatography, which allows purification of highly polar compounds using aqueous media.
- Companies like Mearck have changed their chemical disposal policy, and retaining chemicals with long-term stability rather than discarding all chemicals after three years, thereby saving the cost on disposal.
- Merck has created a green chemistry e-learning course and a green chemistry toolbox. Merck's green chemistry toolbox includes a process mass intensity (PMI) and analytical method volume intensity total solvent consumption calculator, solvent selection guide, pathway to greener solvents, and a reagent selection guide tool kit for enzymatic and catalytic reactions. This will be beneficial for industries and green chemistry practitioners.
- Recently '*Organic Process Research and Development*' has started not to accept papers with chemical solvents like chloroform, benzene, and other absolutely non-green solvents."
- These steps, hopefully, will be beneficial for the green chemistry practice and in turn, for our environment. Enzymes, no doubt will play an important part to achieve the sustainability by performing environmental benign chemical practices.

7. The Future Challenges

Sustainable development is now globally accepted by governments, industry and the public as a necessary goal for achieving societal, economic and environmental objectives. For this, green chemistry has a key role to play in maintaining and improving our quality of life, the competitiveness of the chemical industry and the natural environment. This role for chemistry is to be recognized by government, the public and the industry. In general chemicals, chemistry and chemists are actually seen by as causes of the problems. So chemists need to design such chemical processes and products which are able to preserve efficacy of the function while reducing toxicity. Chemists design new molecules and new materials. Green Chemists have to make sure that the things that we make not only do what they're supposed to do, but they do it safely. In brief it's not only important *how* chemists make something, it's also important that *what* they make isn't harmful. In green chemistry making safe, non-toxic products is the major goal. As a part of the search for safer catalysts, and reaction and product design and optimization, enzymes are looked as a future solution for the environmental hazards.

8. Conclusion

From the beginning in early 1990s Green chemistry has grown from a small idea into a new approach for scientific environmental protection measure. Green chemistry procedures, can minimize the waste of materials, maintain the atom economy and prevent the use of hazardous chemicals. Scientists and researchers, chemical and pharmaceutical companies across the globe are working towards discovering and designing new reagents, new synthesis, new reaction pathways and procedures which are less harmful for environment and more economical. They need to be encouraged to consider the principles of green chemistry while designing the processes and choosing reagents.

Green Chemistry is now a global approach which is contributing to sustainable development through application and extension of its principles. Great efforts are still putting in to design green process starting from and resulting in non-polluting materials. It is a challenge for the future chemical industry research to design research and to discover safer products and processes. Enzymatic reactions and conversion are seen as a hope for these objectives. The use of enzymes as effective catalysts working under mild conditions results in significant savings in resources such as energy and water for the benefit of both the industry as well as the environment. Enzymatic processes are becoming better financial and ecological alternative to other traditional processes by virtue of being cost effective and more environmental friendly.

The success of green chemistry depends on good quality of education and training of a new generation of chemists. So it is necessary at all levels of chemical education to make this new generation familiar with this new 'Green' aspect of chemistry aiming for environment protection.

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