Dipankar et.al / UJPSR / 2 (1), 2016, 35-42
e ISSN: 2454-3764
Print ISSN: 2454-3756

GREEN CHEMISTRY - A NOVEL APPROACH

Arka Roy, Janmojoy Paul, Josef Yakin, Sibabrata Paul, Dipankar Nath*

Department of Pharmaceutical Chemistry, Himalayan Pharmacy Institute, Majhitar, Rangpo, E. Sikkim – 737136, ***INDIA***

ARTICLE INFO:
Article history:
Received:
04 January 2016
Received in revised form:
09 February 2016
Accepted: 10 March 2016
Available online: 10 May 2016

Corresponding Author:

***Mr.* Dipankar Nath**
Deptt. of Pharmaceutical chemistry
Himalayan Pharmacy Institute
Majhitar, E. Sikkim, ***INDIA***
Email: *dipankarnath0@gmail.com*
Phone: *+91-7063682040*

Abstract

Green chemistry is the environment friendly alternative approach which substitutes the use of hazardous and toxic substances. In the edge of twentieth century chemistry has developed its root to a new generation, but also it created so many problems which affecting the environment as well as the human beings. So to overcome the situation a new trend of chemistry has evolved that has the capability to overcome the threats. Thus all the principles of green chemistry, the 12 principles are the ones, by which chemists and technicians can fulfil the requirement of the environment and the society for the betterment of the chemical synthesis in industries and also in our day-to-day life which, substitutes problematic chemical synthesis and improves the environmental human health conditions.

Key words
Green chemistry,
Principles, Solvents, catalyst, atom economy.

INTRODUCTION

The "Green Chemistry" concept was 1st introduced in early 1990's by the US Environmental Protection Agency (EPA) and was soon adopted by mass-media as the new approach in chemistry as substitute to the pollute-and-then-clean up approach considered the common industrial practice. Early definition of the subject is still quoted as "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." The "Green Chemistry" now a day's covers a much broader range of issues, as well as use and production of 'better' chemicals with less waste, it also involves reducing other associated environmental impacts, in particular reducing the amount of energy used in chemical processes **[1]**. The Green Chemistry revolution has provides an enormous number of opportunity to discover and apply new synthetic approaches using alternative feedstock; eco friendly reaction conditions, energy minimization and the design of less toxic and inherently safer chemicals. During, 20th century, chemistry has changed the living & the greatest benefits came from pharmaceutical industries by the development of organic medicinal molecules. Green chemistry is designed to eliminate negative environmental impacts as the use and production of chemicals involves reduced waste products, non-toxic components & improved efficiency. Green chemistry is not a particular set of technologies, but an emphasis on design of chemical product and processes. The approach gives off environmentally beneficial alternatives to most hazardous chemicals and processes and promotes the pollution prevention **[2]**.

Dipankar et.al / UJPSR / 2 (1), 2016, 35-42
e ISSN: 2454-3764
Print ISSN: 2454-3756

PRINCIPLE

Green chemistry is a highly effective approach to pollution prevention due to innovative scientific solutions to real-world environmental situations. The following 12 principles provides a way to chemists to implement green chemistry.

They are as follows:

PREVENTION

ATOM ECONOMY

LESS HAZARDOUS CHEMICAL SYNTHESIS

DESIGNING SAFER CHEMICALS

SAFER SOLVENTS AND AUXILIARIES

DESIGN FOR ENERGY EFFICIENCY

USE OF RENEWABLE FEEDSTOCKS

REDUCE DERIVATIVES

CATALYSIS

DESIGN FOR DEGRADATION

REAL-TIME ANALYSIS FOR POLLUTION PREVENTION

INHERENTLY SAFER CHEMISTRY FOR ACCIDENT PREVENTION

PREVENTION

It is better to prevent waste rather than to treat or clean it after its creation. Waste minimization involves the reduction of waste toxicity by reducing the volume or quantity of highly toxic chemical constituents by substitution, recycling, recovery and reuse. Waste reduction possibilities,

Inputs:

eco friendly solvents,

high purity reagents,

recyclable auxiliaries,

less hazardous materials.

Production:

change time

temperature and pressure,

reactor types,

mixing, heat transfer.

Discharges:

Reduce water volume,

improved scrubbers,

waste water cleanup,

mineralization of organics.

By-products

Maximize use,

Research and development,

Marketing,

Site integration

ATOM ECONOMY

Synthetic methods are designed to maximize the incorporation of all materials used in the processing of final product. The concept of atom economy was developed by BARRY TROST of Stanford University (US). This includes the elimination of non-renewable resources, minimize waste and reduce number of steps in chemical synthesis. The atom economy can be calculated as:

Atom economy- % atom economy = $MW_{(desired\ product)}/MW_{(all\ reactants)} \times 100\%$

Reaction yield- % yield= (actual quantity of product achieved) / (theoretical quantity of products achievable) x 100

LESS HAZARDOUS CHEMICAL SYNTHESIS

Synthetic methods should be designed for use and generation of substances with little or no toxicity to humans as well as environment. Methodologies are designed as such that chemicals and by-products are less harmful to human health & environment. One of the example is the formation of alkenes by safe Grubbs catalyst (very less waste) rather than Witting reaction **[3, 4]**.

Dipankar et.al / UJPSR / 2 (1), 2016, 35-42
e ISSN: 2454-3764
Print ISSN: 2454-3756

DESIGNING SAFER CHEMICALS

Chemical products should be designed to affect their desired function along with minimizing toxicity that reduces the potential risk to human health and environment; decrease production cost and site remediation. As for that, use public transport instead of own vehicle to reduce co_2 emission; use recyclable paper to minimize the burden on natural resources. Develop efficient methods for conversion of solar energy to chemical and electrical energy to avoid nuclear plants which produces nuclear waste, gaseous emission and chemical pollutants **[5]**.

SAFER SOLVENTS AND AUXILIARIES

The use of auxiliary substances (e.g. solvents, separation agents etc) should be made unnecessary. The idea of 'green' solvent is to minimize the environmental impact caused by chemical production. Many organic solvents like benzene, chloroform, toluene are volatile organic compounds (VOC) in industrial applications, increases risk of fire & explosion and also facilitate air pollutants causing ozone depletion, photochemical smog and global warming **[6]**. In green chemistry five main solvent systems are considered as 'green'. They are- solvent less systems, water, ionic fluids, fluorous solvents and supercritical fluids **[7]**.

DESIGN FOR ENERGY EFFICIENCY

Energy required for chemical processes has to be recognized for environmental and economic impacts & has to be minimized. Synthetic methods should be conducted at ambient temperature and pressure. Heavy consumption and future demand of energy based on petroleum and other depleting resources has created a great concern in the community. The solution lies in designing energy efficient processes and generation of alternative source of energy. Chemists are designing reactions that can be done at moderate temperature by using catalysts or other methods, thus reducing demand of more energy.

USE OF RENEWABLE FEED STOCKS

A raw material or feed stock should be renewable rather than depleting. Renewable feed stocks are often made from agricultural products or from wastes of other processes. Whereas depleting feed stocks are made from fossil fuels or mined. Significant efforts are made to develop renewable feed stocks to make fuels and chemicals; related products are obtained from natural resources other than petroleum and depleting resources. Bio-based plastics PLA (polylactic acid) is being made from renewable feed stocks such as corn and potato waste **[8, 9]**.

Table 1: Biomass conversion and bio refinery

Inputs	Building	Outputs(conversion)
Corn	Starch	Butadiene
Potatoes	cellulose	Organic acid
Sorghum	lignin	Furfural
Apple pomace	Suberin	Resorcinol
Beet molasses	chitin	Levulinic acid
Sugar cane	Glycerol & oils	Levoglucosan
Wood residues	Poly hydroxy alkanoate	Per acetic acid

Dipankar et.al / UJPSR / 2 (1), 2016, 35-42
e ISSN: 2454-3764
Print ISSN: 2454-3756

REDUCED DERIVATIVES

Unnecessary derivatization (use of blocking groups, prote-ction/deprotection and temporary modification of physical / chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste. In many traditional chemical reactions, multistep syntheses were designed to employ "protecting groups" that temporarily blocks the reactivity of specific functional group until a deprotecting group removes it. Unnecessary derivatization are minimised or avoided from environmental impact due to more waste production. A non-covalent protecting group was introduced as co-crystal that minimizes lots of waste, thus making the process green **[10]**.

CATALYSIS

Catalytic reagents are superior to stoichiometric reagents. Catalytic chemistry is one of the most important aspects of eco-friendly chemistry that promotes most green chemistry goals such as energy efficiency, lower energy use, higher yields, attaining high levels of selectivity at minimal waste through biocatalysts. Catalysis for this central role referred to as the foundation pillar of green chemistry **[11]**.

DESIGN FOR DEGRADATION

Chemical products should be designed as such that at the end of chemical reaction they break down to innocuous degradation products and don't persist in the environment. Not only the products and materials should be obtained from renewable sources but also they should not persist in the environment. Simple green products are designed to provide cleaning function with chemicals which are non-toxic and biodegradable.

REAL TIME ANALYSIS FOR POLLUTION PREVENTION

Analytical methodologies are developed for allowing real-time, in-process monitoring and control over the hazardous substances. Two aspects of this principle are time and material. Real-time analysis is the process of "checking the progress of chemical reactions as it occurs". Improve the analytical techniques for less material consumption **[12, 13]**.

INHERENTLY SAFER CHEMISTRY FOR ACCIDENT PREVENTION

Substances and form of substances for a chemical process has to be chosen to minimise the chemical accidents, which includes releases, explosions and fires. The Bhopal Gas Tragedy (1984) in India was the worst reminder of industrial tragedy, 40 tons of methyl isocyanate (MIC) accidentally released from holding tank which was over-heated at Union Carbide Pesticide plant. There are some diseases becomes famous by the discharge of poisonous pollutants from industries, were MINAMATA DISEASE (mercury poisoning), Itai-Itai disease (cadmium poisoning), Methaemoglobinaemia (excessive amount of nitrogen fertilizers) etc. **[13].**

SOLVENTS USED IN GREEN CHEMISTRY

Solvents generally used in chemistry are known as Auxiliary Substances (solvents, separating substances). The use of the Auxiliary Substances should be avoided as far as possible, though if used these solvents should not have any harmful effect to the environment. The main aim for the use of green solvents is to reduce the impact of the solvents to the environment and human where it is used. Solvents such as benzene, toluene, and chloroform, pure alcohol etc are widely appreciated for the use in chemistry where this solvents have a volatile nature, thereby increasing the risk of fire and explosion and also affect the atmosphere by depletion of the ozone layer, photochemical smog and global warming **[14]**. According to some case studies methanol-water or ethanol-water is more favourable to environment then pure alcohol or propanol-water mixture.

Dipankar et.al / UJPSR / 2 (1), 2016, 35-42
e ISSN: 2454-3764
Print ISSN: 2454-3756

The solvents to be used should be non-toxic, low price, large availability and renewable **[15]**. The most popular green solvents are water, supercritical carbon dioxide, and ionic liquids. All three have their benefits and drawbacks.

- Water is abundant, non-toxic, and inexpensive, but it is a poor solvent for most organic compounds and it is difficult to remove.
- Supercritical carbon dioxide is abundant, dissolves in most organic solvents and can be removed easily, but it requires a large energy input to generate the pressure needed.
- Room temperature ionic liquids are non-flammable, non-volatile, and easy to recycle, but they are made from petroleum and are toxic to aquatic organism **[16]**.The development of Green Chemistry redefines the role of solvents. The principle focuses the use of solvents which are less hazardous or can be recycled. The great threat to the environment is the use of organic solvents in day to day synthesis.

Water

Water has the capacity to replace toxic and hazardous solvents and found to be very effective in many organic reactions. An efficient method for the synthesis of chromeno-isoxazole/isoxazolines under water conditions has been described. Hydrolysis of hydrophobic glycidyl ether in pressurized water media can afford the corresponding glycerol in good to excellent selectivity within several minutes without a catalyst. Selectively efficient aerobic oxidative iodination of ketones in aqueous media has been achieved by using molecular iodine as the iodine atom source, air as the terminal oxidant and sodium nitrite as the catalyst **[17]**.

Glycerol

Glycerol has been recently proposed as valuable green solvent. Glycerol combines the advantages of both water (low toxicity, low price, large availability, renewability) and ionic fluids (high boiling point, low vapour pressure) and creates innovative solutions to the substitution of the conventionally used volatile organic solvents. Beside solubility of reactants & catalysts and separation of products glycerol provides other benefits such as catalyst recycling. Glycerol derivatives, consisting of over sixty families of 1,3-dialkoxy-2-propanols and 1,2,3-trialkoxypropanes. Both are symmetrically and un-symmetrically substituted at terminal positions are being synthesized and used as green solvents.

Ionic liquids

Ionic liquids comes in two forms, simple salts made of single anion and cation and binary ionic liquids. (EtNH3)(NO3) is a example of simple salt where as mixture of aluminium(III) chloride & 1,3-dialkylimidazolium chlorides contains several ionic species and their melting point & properties depends on their mole fractions. Some room temperature ionic liquids such as BMIM-PF6 (1-Butyl-3-Methylimidazolium hexafluorophosphate) are used as replacement for conventional organic solvents in multiphase bioprocess reactions which includes liquid-liquid extraction of antibiotic erythromycin and two phase biotransformation processes. A very common organic reaction, Friedel-Craft alkylation occurs smoothly & efficiently in chloroaluminate(III) ionic liquids. Many commercially important molecules has been synthesized by Friedel-craft acylations using these ionic liquids. Ionic liquids with a pyridinium cation having an ester side chain moiety can be prepared from either pyridine or nicotinic acids which are biodegradable **[18]**.

Dipankar et.al / UJPSR / 2 (1), 2016, 35-42
e ISSN: 2454-3764
Print ISSN: 2454-3756

Supercritical CO_2

Supercritical CO_2 is a viable alternative but its use has been restricted by its limited solvent power. Beyond a specific temperature and pressure CO_2 becomes a supercritical fluid, a state that is neither a gas nor a liquid, but has properties of both, known as critical point. The specific properties of $ScCO_2$ make it an interesting "green" replacement for organic solvents, which are often less than ideal owing to their acute toxicity, ecological hazards or difficulty with disposal and recycling. Sc-CO_2 has applications in diverse areas as the dyeing and cleaning of fibres and textiles. Polymerization and polymer processing, purification and crystallization of pharmaceuticals, and last but not the least as a reaction medium for chemical synthesis **[19]**.

CATALYST

A green catalyst plays an important role in chemical processes by replacing reagents, enabling more efficient processes, reducing the environmental impacts and reducing cost. This can be done by designing the appropriate cheap, readily preparable, reducible and environment friendly catalysts. Some of the catalysts are used conveniently are chloroauric acid, clay-supported zinc chloride (clayzic), enzymes as biocatalysts. Biocatalysts and biocatalysis is an emerging tool in green technologies. Enzymes are highly efficient with regioselectivity and stereoselectivity. Conduction of reaction in water under ambient condition, both the use of organic solvents and energy input can be minimized **[20]**.

GREEN CHEMISTRY IN PHARMACEUTICALS

Pharmaceutical companies can influence and improve the environmental performance with utilizing green chemistry. Green chemistry is being employed to develop the revolutionary drug delivery methods that are more effective and less toxic and could benefit millions of patients. Phosphoramidite-based, solid-phase synthesis of antisense oligonucleotides has been modified to accommodate principles of green chemistry by eliminating the use and generation of toxic materials and allowing reuse of valuable materials such as amidites, solid-support and protecting groups, thus improving the atom economy and cost-efficiency. Anastas et al has described synthesis of Naproxen with chiral metal catalyst containing BINAP [2,2'bis(diphenylphosphino)-1,1'-binaphthyl] ligand with better yields. This chiral ligand is widely used in asymmetric synthesis. Many forward-looking companies are embracing green chemistry, not only to protect the environment but also to create better public relations. In many companies, the cost of dealing with environmental regulations often exceeds their expenditure for research. Thus, green chemistry is not only good for environment but also for the industry **[21]**.

GREEN CHEMISTRY IN EDUCATION

Convincing all the chemists to think about environment friendly manner starts with education. The idea of including Green Chemistry in chemistry education was first put forward in 1994. A complete course was shortly described in 1995 by Collins. Few Green chemistry textbooks have also been published (Ahluwalia and Kidwai, 2003). Both Environmental Protection Agency (EPA) and American Chemical Agency (ACS) have recognized the importance of bringing Green Chemistry to the class room and the laboratory. Together they have launched a significant campaign to develop Green Chemistry educational materials and to encourage the 'greening' of the chemistry curriculum (ACS, 1998; US-EPA). The green chemistry program should lead to sustainability by designing and using the methods in which natural raw materials will be economically processed, rational usage of energy sources, elimination of hazardous gaseous, liquid and solid wastes and by introduction of safety products for man. The alternative green chemistry activity includes several suggestions. They are as follows:

- Hosting a Green Chemistry speaker

Dipankar et.al / UJPSR / 2 (1), 2016, 35-42
e ISSN: 2454-3764
Print ISSN: 2454-3756

- 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 sessions on campus
- Distributing a Green Chemistry Newsletter to the local community
- Designing a green Chemistry web page

GREEN CHEMISTRY IN DAY-TO-DAY LIFE

Dry Cleaning of Cloths- Perchloroethylene (PERC), $Cl_2C=CCl_2$ is commonly being used as a solvent for dry cleaning. It is now known that PERC contaminates groundwater and is a suspected carcinogen. A technology, known as Micell Technology developed by Joseph De Simons, Timothy Romark, and James McClain made use of liquid CO_2 and a surfactant for dry cleaning clothes, thereby replacing PERC. Dry cleaning machines have now been developed using this technique. Micell Technology has also evolved a metalcleaning system that uses CO_2 and a surfactant, thereby eliminating the need of halogenated solvents. Versatile leaching Agent- Paper is manufactured from wood which contains 70% polysaccharides & 30% lignin. Lignin must be completely removed for good quality paper. Initially, lignin is removed by placing small B chipped pieces of wood into a bath of sodium hydroxide (NaOH) and sodium sulphide (Na_2S). About 80-90% of lignin gets decomposed by this process. The remaining part is substituted by reaction with chlorine gas(Cl_2). But it causes environmental problems. Chlorine reacts with aromatic ring of lignin to form dioxins such as 2,3,4-tetrachloro-P-dioxin and other chlorinated furans which are potencial carcinogens and causes other health problems. Other bleaching agents like hydrogen per oxide (H_2O_2), ozone (O_3) or oxygen (O_2) also does not give the desired results. A versatile agent has been developed by Terrence Collins of Camegie Mellon University which involves the use of hydrogen peroxide as a bleaching agent in the presence of some activators known as the TAML activators **[22]**.

Table 2: Examples of implementation of green chemistry principles in practice

Nr	Principle	Example
1	Prevention	Use of solvent-less sample preparation technique
2	Atom economy	Hydrogenation of carboxylic acids to aldehydes using solid catalysis
3	Less hazardous chemical synthesis	Adipic acid synthesis by oxidation of cyclohexene using hydrogen peroxide
4	Designing safer chemicals	New, less hazardous pesticide (e.g.-Spinosad)
5	Safer solvents and auxiliaries	Supercritical fluid extraction,Synthesis in ionic liquids
6	Design for energy efficiency	Polyolefins-polymer alternative to PWC
7	Use of renewable feedstocks	Production of surfactants
8	Reduce derivatives	On-fiber derivatization or derivatization in solution in sample preparation
9	Catalysis	Efficient Au(III)-catalyzed synthesis of b-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 wastewater monitoring
12	Inherently safer chemistry for accident prevention	Di-Me carbonate(DMC) is an environmentally friendly substitute for Di-Me sulfates and Me halides in methylation reactions

Dipankar et.al / UJPSR / 2 (1), 2016, 35-42
e ISSN: 2454-3764
Print ISSN: 2454-3756

CONCLUSION

Combination of technological progress with environment protection is the new challenge of this new era. Chemists will play a key role in the realization of the conditions for a sustainable development and green chemistry may be their winning strategy. Green chemistry has grown from a small idea into a new approach to the scientifically based environmental protection. By using green chemistry procedures, we can minimize the waste of materials, maintain the atom economy and prevent the use of hazardous chemicals. Green chemistry is not a new branch of science. It is a new approach that through application and extension of the principles of green chemistry can contribute to sustainable development.

REFERRENCES

1. *Anastas, P.T. and T.C. Williamson, 1998. Green chemistry: frontiers in benign chemical syntheses and processes. New York, Oxford University Press, pp: 2.*

2. *Tundo, P., P. Anastas, D.S. Black, J. Breen, T. Collins, S. Memoli, J. Miyamoto, M. Polyakoff and W. Tumas, 2000. Synthetic pathways and processes in green chemistry. Introductory overview. Pure Appl. Chem., 72(7): 1207-1228.*

3. *Anastas, P.T. and J.C. Warner, 1998. Green Chemistry, Theory and Practice, Oxford University Press, Oxford, pp: 30.*

4. *Walter L. Green Solvents–Progress in science and application. Green Chem 2009;11:603*

5. *Christian CF and Konrad H.What is a green solvent? A comprehensive framework for the environmental assessment of solvents. Green Chem 2007;9:927–934 11*

6. *Glaze WH. Sustainability engineering and green chemistry. Env Sci Technol 2000;34:449A*

7. *Winterton N. Twelve moregreen chemistry principles? Green Chem 2001;3:G73–G75*

8. *Seyler CC, Hellweg S, Bruder B et al. Waste-Solvent Management as an Element of Green Chemistry: A Comprehensive Study on the Swiss Chemical Industry. Ind Eng Chem Res 2006;45:7700–7709 .*

9. *Kidwai, M., Mohan, R. and , Saxana, R. 2003. Russ. Chem. Bull. Int. Ed., 52 (11)pp. 2457-2460.*

10. *Hoyle,W. and Lanchester,M.2001. Royal Society of Chemistry.*

11. *Khurana, J.M. 1990. Chemistry Education, pp. 24-29.*

12. *V. K. Ahluwalia and M. Kidwai, New Trends in Green Chemistry, Anamaya Publishers, New Delhi, 2004.*

13. *B. M. Trost, Atom economy—A challenge for organic synthesis: Homogeneous catalysis leads the way. Angew Chem Int Ed.,1995, 34, 259.*

14. *J. M. Thomas, R. Raja, Aust. J. Chem., 2001, 54, 551.*

15. *Roger MS. Superheated water:the ultimate green solvent for separation science. Anal Bioanalchem 2006;385:419-421*

16. *NICOLAS N., BENVEGNU T., PLUSQUELLEC D. Surfactants from renewable resources. Actualite Chimique 1112, 70, 2002.*

17. *Mustafa JR, Veerababurao K, Chun-Wei K, RajuBR and Ching-Fa Y. On-water synthesis of chromeno-isoxazoles mediated by [hydroxy(tosyloxy)iodo]benzene(HTIB) Green Chem 2010;12:1090-1096*

18. *Yanlong G and Francois J. Glycerol as a sustainable solvent for green chemistry. Green Chem 2010;12:1127-1138*

19. *R. A. Sheldon, Green solvents for sustainable organic synthesis: State of the art. Green Chem., 2005,7, 267.*

20. *G. Jesson,W. Leitner, Chemical synthesis using supercritical fluids, Wiley-VCH Weinheim, 1999.*

21. *Anastas PT,Lauren BB,Mary MK, Tracy CW.The role of catalysis in the design, development and implementation of green chemistry.Catalysis Today.2000;55(1):11-22*

22. *Wardencki, W., J. Curyo and J. Namisnik, 2007. Trends in solventless sample preparation techniques for environmental analysis Journal of Biochemical and Biophysical Methods, 70(2): 275-288.*