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Review Article

Potentiality of Green Chemistry for Future Perspectives

Bina Rani[1], Raaz Maheshwari[2*], AK. Chauhan[2] and Upma Singh[3]

[1]Department of Engineering Chemistry & Environmental Engineering, PCE, Sitapura,
Jaipur, Rajasthan, India.
[2]Department of Chemistry, SKGC, Sikar, Rajasthan, India.
[3]School of Vocational Studies & Applied Sciences, Gautam Buddha University, Greater
Noida, Uttar Pradesh, India.

ABSTRACT

Chemistry brought about medical revolution till about the middle of twentieth century in which drugs and antibiotics were discovered. The world's food supply also increased enormously due to the discovery of hybrid varieties, improved methods of farming, better seeds, use of insecticides, herbicides and fertilizers. The quality of life on earth became much better due to the discovery of dyes, plastics, cosmetics and other materials. Soon, the ill effects of chemistry also became pronounced, main among them being the pollution of land, water and atmosphere. This is caused mainly due to the effects of by-products of chemistry industries, which are being discharged into the air, rivers/ oceans and the land. The hazardous waste released adds to the problem. The use of toxic reactants and reagents also make the situation worse. The pollution reached such levels that different governments made laws to minimise it. This marked the beginning of *Green Chemistry* by the middle of 29th century. Green Chemistry is defined as environmentally benign chemistry. The synthetic schemes are designed in such a way that there is least pollution to the environment. As on today, maximum pollution to the environment is caused by numerous chemical industries. The cost involved in the disposal of the waste products is also enormous. Therefore, attempts have been made to design synthesis for manufacturing processes in such a way that the waste products are minimum, they have no effect on the environment and their disposal is convenient. For carrying out reactions it is necessary that the starting materials, solvents and catalysts should be carefully chosen. For example Benzene (C_6H_6) as a solvent must be avoided at any cost since it is carcinogenic in nature. If possible, it is best to carry out reactions in the aqueous phase. With this view in mind, synthesis methods should be designed in such a way that the starting materials are consumed to the maximum extant in the final product. The reaction should also not generate any toxic by-products.

Keywords: Safer chemicals, Hazardous wastes, Chemical education, Environmental objectives.

INTRODUCTION

The Green Chemistry revolution provides an enormous number of opportunity to discover and apply new synthetic approaches using alternative feedstock; Ecofriendly reaction conditions, energy minimization and the design of less toxic and inherently safer chemicals. The origin and basis of Green Chemistry for achieving environmental and economic prosperity is inherent in a sustainable world. One important element of sustainable chemistry is commonly defined as the chemical research aiming at the optimization of chemical processes and products with respect to energy and material consumption, inherent safety, toxicity, environmental degradability, and so on. While considering progress has been made in environmental chemistry, Green Chemistry, and the environmental assessment of chemical products, however, the societal aspect of sustainable chemistry remains to be fully recognized in all branches of chemical research. One prerequisite for this is the inclusion of sustainable chemistry into chemical education from the very beginning.

Green Chemistry is the utilization of set of principles that reduces or eliminates the use or generation of hazardous substances in design, manufacture and application of chemical products. In practice, Green Chemistry is taken to cover a much broader range of issues than the definition covers (Lancaster, 2000). As well as using and producing better chemicals with less waste, Green Chemistry also involves reducing other associated environmental impacts (Hoyle and Lancaster, 2001), including reduction in the amount of energy used in chemical processes. Green Chemistry is not different from traditional chemistry in as much as it embraces the same creativity and innovation than has always been central to classical chemistry. However, there lies a difference in that historically synthetic chemists have not been seen to rank the environment very high in their priorities. But with the increase in environmental consciousness throughout the world, there is a challenge for chemists to develop new products, processes and services that achieve necessary social, economical and environmental objectives. Since the types of chemicals and the types of transformations are much varied, so are the Green Chemistry solutions that have been proposed. Anastas and Warner (!998) developed 'The twelve Principles of Green Chemistry' that serve as guidelines for practising chemists in developing and assessing how green a synthesis, compound, process or technology is.

Basic Principles of Green Chemistry

- Prevention of waste/ by-products
- Maximum incorporation of the reactants (starting materials and reagents) into the final product
- Prevention or minimization of hazardous products
- Designing of safer chemicals
- Minimum energy requirement for any synthesis
- Selecting the appropriate starting solvents
- Selecting the most appropriate solvent
- Whenever possible avoid the use of protecting group
- Whenever possible prefer use of catalysts
- Biodegradable products
- Design manufacturing plants so as to eliminate the possibility of accidents during operations
- Strengthening of analytical techniques to control hazardous compounds

INDUSTRIAL INTEREST IN GREEN CHEMISTRY

Many forward-looking companies are embracing Green Chemistry, not only to protect the environment and to create good public relations, but also because it is often beneficial to the bottom line It is also estimated to cost US industries between $ 100 and $ 150 billion per year to comply to environmental regulations. In addition, cleaning up hazardous waste sites will cost hundreds of billion of dollars. In many companies, the cost of dealing with environmental regulations often exceeds their expenditure for research. Larger companies budget close to $ 1 billion per year for environmental compliance. If a company can significantly reduce these expenditure, then these funds can be spent in more productive areas and result in an improved bottom line. Thus, Green Chemistry (pollution prevention) is not only good for the environment but also for industry (Wilkinson, 1997).

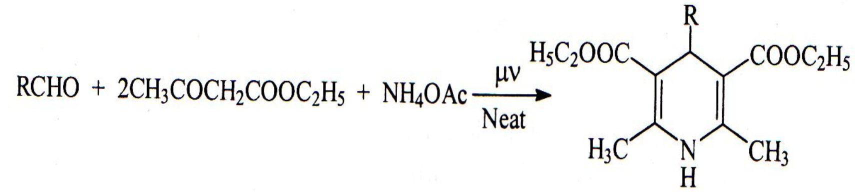
GREEN CHEMISTRY IN EDUCATION

Convincing chemists to think in an environmentally friendly manner begins with education. The idea of including Green Chemistry in chemistry education was first put forward in 1994. A complete course was described shortly thereafter (Collins, 1995). Few Green chemistry textbooks have also been published (Ahluwalia and Kidwai, 2003). Graduates, post graduates, teachers and researchers will find these books of immense use. 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). Student involvement in Green Chemistry principles and practices is essential to the integration the environmentally benign technologies in academia and industry. ACS Student Affiliate Chapters may be recognized as "green" chapters by engaging in at least three Green Chemistry activities during the academic year. Suggestions for these activities include:

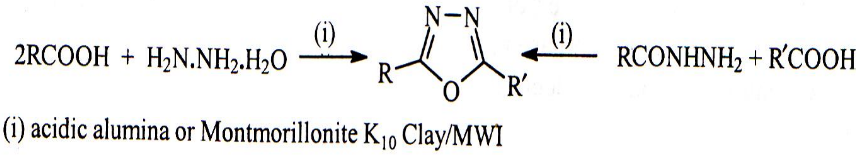
- Hosting a Green Chemistry speaker
- Organizing an interdisciplinary Green Chemistry workshop on campus
- Working with a local company on a Green Chemistry project
- Developing a Green Chemistry activity with a local school
- Converting a current laboratory experiment into a greener one
- Organizing a Green Chemistry poster sessions on campus
- Distributing a Green Chemistry Newsletter to the local community
- Designing a green Chemistry web page

ENERGY CONSERVATION

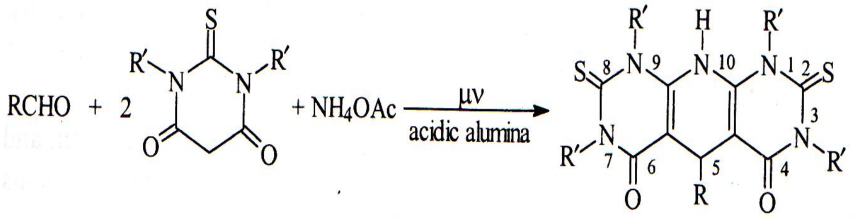
Energy conservation and consumption has long been known to produce a major environmental effect. Chemistry and chemical transformations has long been known to produce a major role in capturing and converting substances into energy as well as converting existing sources of energy into a form that is usable to society. Microwave irradiation in the solid state (Varma, 1999) is a technique that is being utilized to affect chemical transformations rapidly, in contrast to those that have classically been conducted in liquid solutions. Solvent-free microwave assisted reactions (Kidwai, 2001) provide an opportunity to work with open vessels, thus, avoiding the risk of high pressure and increasing the potential for scale up of such reactions. The practical feasibility of microwave assisted solvent free synthesis has been demonstrated in various useful transformations (Csiba et. al., 1993) and in the synthesis of heterocyclic systems (Kidwai et. al., 2003) **[Scheme 1-3].**



Scheme 1



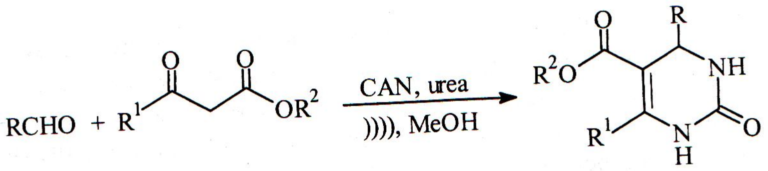
Scheme 2



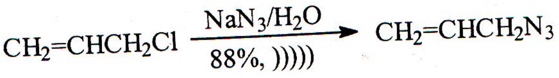
Scheme 3

The microwave technique has shown distinct advantages in not requiring prolonged heating to carry out a reaction.

Ultra sound is a relatively new way of introducing energy into chemical systems (Khurana, 1990). It has been used to enhance reaction rates (Yadav, 2000) in a large number of classical reactions [**Scheme 4**]. Though the use of phase transfer catalysis in organic aqueous biphasic systems is well known to catalyse heterogeneous liquid-liquid reactions, ultra sound is much more effective in these reactions because ultrasonic waves generate extremely fine emulsions which results in very large interfacial contact areas between the liquids and a corresponding dramatic increase in the reactivity between dissolved species [**Scheme 5**].



Scheme 4



$$CH_2{=}CHCH_2Cl \xrightarrow[88\%,\ )))))]{NaN_3/H_2O} CH_2{=}CHCH_2N_3$$

Scheme 5

The problems associated with waste disposal of solvents and excess chemicals have been overcome by performing reactions without solvent under microwave irradiation or ultrasound. Heterogeneous organic reactions have also proven useful to chemists. These reactions are affected by the reagent immobilized on the porous solid supports and have advantages over the conventional solution phase reactions because of good dispersion of active reagent sites, associated selectivity and easier work up.

SUSTAINABLE CHEMISTRY: STARTING POINTS AND PROSPECTS

Sustainability is significantly determined by how we manipulate matter within the economy, the inventive leadership of chemists is vital to its future (Collins, 2000). Sustainable chemistry should also address the societal aspect of sustainability, with respect to scientific research; the societal aspect is designed by two requirements:

(a) The assumptions, objectives and implication of chemical research and its technical application should be made more transparent to various societal actors.
(b) Uncertainty and ignorance should be treated explicitly in the course of scientific research.

CURRENT STATUS

Since 1991, Green Chemistry has grown into a significantly internationally engaged focus area within chemistry. Research programs and centers located in America, Europe, Asia/Pacific and Africa are focusing efforts around the principles of Green Chemistry, the breadth of this research is very wide and incorporates area such as:

I Bio-based Renewables

The utilization of benign, renewable feedstock is needed for addressing the global depletion of resources. Bio-based products hold great promise for achieving the goals of sustainable development and implementing the principles of industrial, ecological and Green Chemistry Achieving a sustainable chemical industry dictates switching from depleting finite sources to renewable feed stock. Research has focussed on both, the micro and molecular levels

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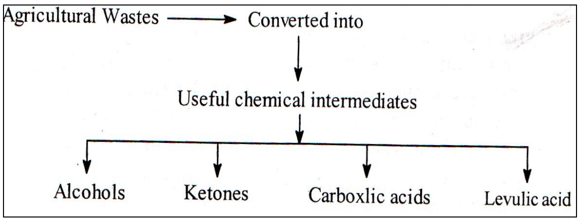


(i) The carbohydrate economy provides a rich source of feedstock for synthesizing commodity (Lynel et. al., 1999). And for example:

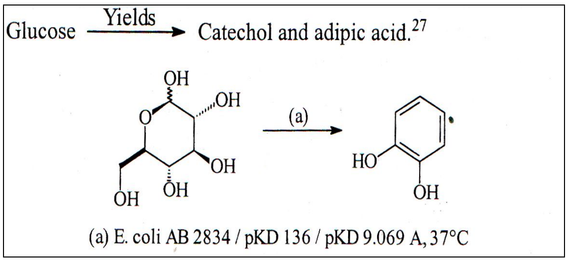
(ii) Shells from crabs and other sea life serve as a valuable and plentiful source of chitin, which can be processed into chitosan a biopolymer with a wide range of potential applications that are being currently explored for use in the oil-drilling industry (Kumar et al., 2000).

(iii) Genetic engineering produces valuable chemical products via non-traditional pathways.

(iv) Glucose $\xrightarrow{\text{Yields}}$ Catechol and adipic acid (Draths and Frost, 1999)

(v) Saccharomyces yeasts convert both glucose and xylose, present in cellulogic biomass, into ethanol (Ho et. al., 2000).

(vi) CO_2 is also a renewable feedstock that has been incorporated into polymers (Chong et. al., 2000).

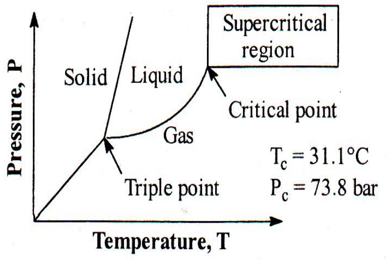


GREEN ENGINEERING EDUCATION FOR SUSTAINABILITY FOR DEVELOPING COUNTRIES

Zujang et.al., 2004, presented a paper of existing philosophy, approach, criteria and delivery of Environmental Engineering (EE) Education (E_3) for developing countries.

- In general EE is being taught in almost all major university major universities in developing countries, mostly under civil engineering degree programmes. The main component of E_3 in near future will remain on basic sanitation in most developing countries, with special emphases on the consumer-demand approach.
- The concept, principles and methodologies of Green Chemistry and green engineering are fundamental in integrating sustainability throughout the system of our chemical enterprise. By incorporating these Green Chemistry approaches in the research and Development, scale up and commercialization stages in industry and by insuring that training of both established and next generation chemists and engineers includes Green Chemistry and engineering , large strides can and are being made sustainability in the chemical industry.
- In order to overcome environmental problems in developing countries, E_3 include integrated urban water management, sustainable sanitation, appropriate technology, cleaner production, waste water minimization and financial framework.

COMPRESSED CO_2: AN ENVIRONMENTALLY FRIENDLY SOLVENT



Phase diagram for CO_2

Many solvents are unpleasant but essential industrial chemicals. Supercritical CO_2 would be viable alternative but its use has been restricted by its limited solvent power. This is about to change.

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.

A. 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.

B. $ScCO_2$ find applications in areas as diverse 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.

C. Most widely used CO_2 philic solubilizers have been polysiloxanes and fluorocarbons. The Beckman group(Sarbau et. al., 2004) has now synthesized a non-fluorous but still highly CO_2 philic polymer, whose solubility in $ScCO_2$, whose solubility in $ScCO_2$ results from a judicious design. The target compound of the Beckman group was copolymer (Polyether polycarbonate group) with copolymers can be easily generated using an Al-catalyst to react propylene oxide (C_3H_6O) with CO_2 itself.

D. Polyether skeleton is highly flexible and has only weak polymer-2 interactions, when carbonate group is introduced. It enhances this flexibility, and therefore the entropy of mixing. At the same time a favourable interaction of the carbonyl group with CO_2 may increase the enthalpy of mining, thereby also improving the solubility of these compounds in CO_2.

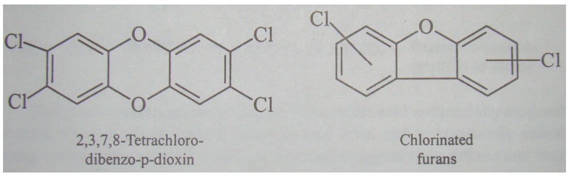
GREEN CHEMISTRY IN DAY-TO-DAY LIFE

1 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 metal-cleaning system that uses CO_2 and a surfactant, thereby eliminating the need of halogenated solvents (Micell Technologies, 1999).

2 Versatile Bleaching Agent

It is common knowledge that paper is manufactured from wood (which contains about 70% polysaccharides and about 30% lignin). For good quality paper, the lignin must be completely removed. Initially, lignin is removed by placing small chipped pieces of wood into a bath of sodium hydroxide (NaOH) and sodium sulphide (Na_2S) [that is how pulp is formed]. By this process about 80-90% of lignin is decomposed. The remaining lignin was so far removed through reaction with chlorine gas (Cl_2). The use of chlorine removes all the lignin (to give good quality white paper) but causes environmental problems. Chlorine also reacts with aromatic rings of the lignin (by aromatic substitution) to produce dioxins, such as 2,3,4-tetrachloro-p-dioxin and chlorinated furans. These compounds are potential carcinogens and cause other health problems.



These halogenated products find their way into the food chain and finally into products like dairy products, pork, beef and fish. In view of this, use of chlorine has been discouraged. Subsequently, chlorine dioxide was used. Other bleaching agents like hydrogen per oxide (H_2O_2), ozone (O_3) or oxygen (O_2) also did not give this the desired results. A versatile agent has been developed by Terrence Collins of Camegie Mellon University. It involves the use of hydrogen peroxide as a bleaching agent in the presence of some activators known as TAML activators (Hall et al., 1999) that as catalysts which promote the conversion of hydrogen peroxide into hydroxyl radicals that are involved in oxidation/ bleaching. The catalytic of TAML activators allows hydrogen per oxide to break down more lignin in a shorter time and at much lower temperature. These bleaching agents find use in laundry and result in lesser use of water.

CONCLUSION

The expansion of Green Chemistry over the course of the past decade needs to increase at an accelerated pace if molecular science is to meet challenges of sustainability. It has been said that the revolution of one day becomes the new orthodoxy of the next Green Chemistry is applied and must involve the successful implementation of more environmentally friendly chemical processes and product design. Most importantly we need the relevant scientific, engineering, educational and other communities to work together for sustainable future through Green Chemistry.

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