Better living through 'Sustainable green chemistry'

Rashmi Sanghi

As the natural resources are used up in the world, chemists and biotechnologists are being asked to come up with innovative ways in which renewable resources can be used to replace non-renewable ones. But there will continue to be a demand for some non-renewable resources. If we wish to make materials that use less resources today, we should try to minimize the amount of raw material that is incorporated in the object. As new materials are developed, new standards must be made to ensure fitness for the purpose of these materials. Analytical chemistry provides the means for ensuring that the material should meet the purpose for which it is designed. For this, green chemistry principles must be applied to the resources industry and raw material use. The concept of green chemistry though widespread in developed countries like US, needs to be implemented in India with a wider vision.

THE society is dependent in many ways on the chemical industry to maintain the current standards of living and improve the quality of our lives – 'better living through chemistry'. The past few decades have been an era of successful chemistry. Developments in water treatment, waste disposal methods, agricultural pesticides and fungicides, polymers, materials sciences, detergents, petroleum additives and so forth, have all contributed to the improvement in our quality of life. But unfortunately all these advances come with a price tag of 'pollution'. Today, with growing awareness, in industry, academia and the general public, of the need for sustainable development, the international chemistry community is under increasing pressure to change current working practices and to find greener alternatives. Scientists and engineers from both the chemical industry and the academic world have made efforts to correct pollution problems by the more extensive use of 'green chemistry' concepts, i.e. development of methodologies and products that are environmentally friendly. As the name implies, the green chemistry[1–3] movement aims to make humanity's approach to chemicals, especially synthetic organic chemicals, environmentally 'benign' or 'sustainable'. 'Organic chemistry textbooks, a generation from now will be unrecognizable compared with today's standard texts', predicts one of the progenitors of what is coming to be called green chemistry.

For better living, what is needed is:

(a) An increasing awareness in industry of the importance of concepts such as waste minimization[4] and atom utilization[5].

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(b) Greater involvement by governments in controlling the use of resources and the productive disposal of waste.

(c) Emergence of other underpinning concepts as general principles which can be used in the conception and execution of synthetic chemistry and in the usage of chemicals produced.

The term green chemistry[6,7] describes an area of research arising from scientific discoveries about pollution and from public perception, in much the same way as the identification and understanding of a deadly disease stimulating the call for a cure. This term, which was coined at the Environmental Protection Agency (EPA) by Paul Anastas, represents the assumption that chemical processes that carry environmental negatives can be replaced with less polluting or non-polluting alternatives. 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, associated with a particular synthesis or process. Thus chemists can greatly reduce risk to human health and the environment.

Green chemistry

Green chemistry, an approach to the synthesis, processing and use of chemicals that reduce risks to humans and the environment, covers the following areas:

- Application of innovative technology to established industrial processes.
- Development of environmentally improved routes to important products.

- Design of new green chemicals and materials.
- Use of sustainable resources.
- Use of biotechnology alternatives.
- Methodologies and tools for evaluating environmental impact.

Green chemistry involves the design and redesign of chemical syntheses[8] and chemical products to prevent pollution and thereby solve environmental problems. The research applications and the anticipated directions for the principles of green chemistry include:

a) Clean synthesis[9] (e.g. new routes to important chemical intermediates).
b) Enhanced atom utilization (e.g. more efficient methods of bromonation).
c) Replacement of stoichiometric reagents[10] (e.g. catalytic oxidation using air as the only consumable source of oxygen).
d) New solvents and reaction media (e.g. use of supercritical fluids[11] and reactions in ionic liquids).
e) Water-based processes and products (e.g. organic reactions in high-temperature water).
f) Replacement for hazardous reagents (e.g. the use of solid acids[12] as replacement for traditional corrosive acids).
g) Novel separation techniques[13,14] (e.g. the use of novel biphasic systems such as those involving a fluorous phase).
h) i) Alternative feedstocks (e.g. the use plant-derived products as raw materials for the chemical industry).
   ii) New safer chemicals and materials[15] (e.g. new natural product-derived pesticides[4] and insecticides[16]).
i) Waste minimization and reduction (e.g. applying the principles of atom utilization and the use of selective catalysts).

In most chemical reactions, the major component is the solvent. Care must be taken to ensure that solvent is chosen to minimize waste generation, both through supporting efficient reaction and facilitating product isolation and recovery. The recent increased awareness of the potentially detrimental effects of organic solvents on the environment, has led to a rapid growth in research into alternative reaction media. The demand for solvents has declined over the past decade due to a combination of environmental concerns and stricter legislation, as well as weak European and Asian economies. The trend from chlorinated solvents towards oxygenated solvents continues. No doubt, the exploration of synthetic possibilities using critical fluid and conditions to yield environmentally-benign manufacturing processes offers new challenges and opportunities. Such fluids avoid many of the problems associated with organic solvents, including flammability, product contamination and the costs associated with solvent disposal. To date, many of these critical fluid[17,18] processes have utilized supercritical CO_2, due to its low cost, attractive critical constants and relative inertness[19].

From the kitchen to the laboratory, 'microwave chemistry' has come up as a boon in disguise for the eco-friendly conscious chemists. The microwave mediated-organic reactions[20,21] take place more rapidly, safely, and in an environmentally friendly manner, with high yields. Very little solvent and even the use of water as a solvent is a big advantage of microwave chemistry. In many cases, microwave-mediated reactions are carried out in dry media on solid support, i.e. without the use of solvent. Therefore the use of toxic and expensive organic solvents can be avoided. Such reactions not only reduce the amount of waste solvent generated, but also the products often need very little or no purification. These processes will hopefully be adapted by big industries as well, thereby contributing to the betterment of the environment.

Within two decades is should be possible to:

- Eliminate nearly 100% of emissions in polymer manufacturing and processing.
- Replace all solvents and acid-based catalysts that have adverse environmental effects with solids, or 'greener alternatives'.
- Achieve 30–40% reduction in waste.
- Reduce more than 50% quantity of plastics in landfills.

Inception of green chemistry in USA

Shortly after passing the Pollution Prevention Act of 1990, The Office of Pollution Prevention and Toxics (OPPT) in USA explored the idea of developing existing chemical products and processes to make them less hazardous to human health and the environment. In 1991, OPPT launched a model research grants programme 'Alternative Synthetic Pathway for Pollution Prevention'. Since then, the green chemistry programme has built many collaborations with academia, industry and other government agencies to promote the development and implementation of innovative chemical technologies for pollution prevention, both in a scientifically sound and a cost-effective manner.

Several awards have been given to processes achieving green chemistry:

(a) For 'catalytic dehydrogenation of diethanolamine' in which a new technique allowed the production of an environmentally friendly roundup herbicide in a less dangerous way. This technology represents a major breakthrough because it avoids the use of cyanide and formaldehyde, is safer to operate, produces high overall yield and has fewer process steps.

(b) For developing a new method of synthesizing ibuprofen in 99% yield, avoiding the usage of large quantities of solvents and wastes associated with the traditional stoichiometric use of auxiliary chemicals when effecting chemical conversions.

(c) For developing processes using carbon dioxide as the blowing agent, for manufacture of polystyrene foam sheet packaging material. This technology allowed elimination of 3.5 million pounds of chlorofluorocarbon blowing agents per year, chemicals that contributed to ozone depletion, global warming and ground level smog.

(d) For designing a safer marine antifouling compound, 'Sea-nine' which degrades far more rapidly than organotins which persist in the marine environment and cause pollution problems.

(e) The problem of persistent pollutants in the environment can be minimized by employing reagents and processes that mimic those found in nature. An award was given for developing a series of activators effective with the natural oxidant hydrogen peroxide. An environmentally benign oxidation technique with widespread applications in the pulp and paper industry and the laundry field, was developed as a result of this work.

(f) Similarly, the synthesis of a pharmaceutical agent is frequently accompanied by the generation of a large amount of waste in the form of reagents, solvents and separation agents, etc. Synthesis of an anticonvulsant drug, whereby roughly 34,000 l of solvent and 300 kg of chromium waste were eliminated per 100 kg of the drug produced, has received an award. The new protocol was developed by combining innovations from chemistry, microbiology and engineering. Minimizing the number of changes to the oxidation state improved the efficiency of the process, while reducing the amount of waste generated. The alternative synthesis presents a novel strategy for producing 5H-2,3-benzodiezepines.

Some recent developments and examples

Chemists from all over the world are using their creative and innovative skills to develop new processes, synthetic methods, analytical tools, reaction conditions, catalysts, etc. under the new green chemistry cover. Some of these are:

- A continuous process and apparatus converts waste biomass into industrial chemicals, fuels and animal feed. Another process converts waste biomass such as municipal solid waste, sewage sludge, plastic, tires and agricultural residues to useful products, including hydrogen, ethanol and acetic acid.
- A method for mass producing taxol by semi-continuous culture of Taxus genus plant.
- A fermentation method for the production of carboxylic acids.
- A method of partially oxidizing alcohol such as methanol to ethers, aldehydes, esters or acids, by using a supercritical fluid mobile.
- A process for producing a fluoropolymer by using supercritical carbon dioxide.
- A cost-effective method of producing ethyl lactate, a non-toxic solvent derived from corn.
- A range of 'organic solvents' that are worker friendly and environmentally sound.
- A new environmentally friendly technology in mixed metals recovery from spent acid wastes has been used to recover zinc and ferrous chloride from pickle liquor.
- The demand for non-ionic surfactants is growing and a new example of this is alkly glycoside, which is made from saccharide. This product can be used as a replacement for alkylaryl sulphonate anionic surfactants in shampoos. Sodium silicate can be used as a more environmentally benign replacement for phosphorus-containing additives in washing powder. Three coconut oil soap bases for liquid cleansing applications have been developed. One of these products has very light colour and low odour, making it suitable for introducing dyes and fragrances.
- Feedstock recycling[22] of plastic wastes into valuable chemicals useful as fuels or raw materials.
- The first bio-pesticide for sugarcane, called *BioCane*[23], has recently been launched in Australia. The product is based on a naturally-occurring fungus that has been cultured on broken rice grains to provide a medium for distribution. Biocane granules are claimed to be particularly effective against greyback canegrub.

Green chemistry in India

The green chemistry wave has reached our country too. We need to work for its betterment by encouraging the practices of green chemistry. Collaborations between industrial and academic partners are important to expedite the transfer of significant green products to the marketplace. For such collaborations to be successful, individuals in these two differently motivated cultures need to work together to advance green science. Governments could undoubtedly facilitate formation of more effective industrial/academic partnerships. Under an agreement with the Green Chemical Institute, University of Delhi has been accepted as an international chapter. The Indian chapter will promote green chemistry through education, information collection and dissemination, research and international collaboration via conferences, workshops, meetings and symposia. As one of the initial activities of the chapter, the Chemistry Department of University of Delhi is organizing an International Symposium on Green Chemistry in January 2001.

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REVIEW ARTICLES

Cancer modulation by glucosinolates: A review

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Glucosinolates (GLS) are a group of plant thioglucosides present in plants of Cruciferae family. They are well known for their toxic effects (mainly as goitrogens) in both man and animals at high doses. In contrast at subtoxic doses, their hydrolytic and metabolic products act as chemoprotective agents against chemically-induced carcinogens by blocking the initiation of tumours in a variety of rodent tissues, viz. liver, colon, mammary gland, pancreas, etc. They exhibit their effect by inducing Phase I and Phase II enzymes, inhibiting the enzyme activation, modifying the steroid hormone metabolism and protecting against oxidative damages. Acid condensation products (like DIM) are more effective than their parent compounds (like I3C). Anticarcinogenesis caused by GLS is reviewed here.

GLUCOSINOLATES (GLS) are a group of plant thioglucosides found among several vegetables. The first crystalline glucosinolate, sinalbin, was isolated from the seeds of white mustard in 1831. Since then, more than 100 different GLS have been characterized. GLS occur mainly in the order Capparales, principally in the families Cruciferae, Resedaceae and Capparidaceae, although their presence in other families has also been reported[1]. Some economically important GLS-containing plants are white mustard, brown mustard, radish, horse radish, cress, kohlrabi, cabbages (red, white and savoy), brussels sprouts, cauliflower, broccoli, kale, turnip, swede and rapeseed[2]. GLS concentration in plants depends on various factors such as variety, cultivation conditions, climate and agronomic practices. Concentrations in a particular plant also vary between different parts of the plant[3]. A considerable amount of research has been conducted to elucidate the toxic effects of GLS in animals. The ingestion of large amounts of GLS-containing feeds may reduce feed intake, cause thyroid gland hypertrophy and reduce levels of circulating thyroid hormones, mainly by inhibiting the iodine uptake by the gland[4–10]. Such effects may adversely affect the productive performance of livestock. Poultry and pigs are more susceptible than cattle,

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