Green chemistry in Indian context – Challenges, mandates and chances of success

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Reckless use of chemicals, careless disposal of chemical wastes causing ecological imbalance, and the lack of premonition became a global threat causing concern to many. Subsequently, a realization of the detrimental consequences has led to the promulgation of several legislations, followed by their implementation to some extent, in the industrially advanced nations like USA, UK, Germany and Japan, for instance. All these and some related problems became a cause of concern which then led to the concept of 'Green chemistry' to crystallize. The concerted effort of the proponents of Green chemistry led to the pronouncement of 12 principles which are now considered as the guiding tenets for working chemists and technologists. To make a lasting impact on the future generations of chemists and policy makers for chemical sciences/technologies, the American Chemical Society (ACS) has been working jointly with the US Environmental Protection Agency (EPA) to provide knowledge and skills to ensure ways that are benign to human habitat and environment. The EPA's Green chemistry Programme has taken the responsibility of developing Green chemistry resource materials for classroom and laboratory uses and encourages their implementation.

In order to emphasize the rightly deserving importance, US Presidential Green chemistry Challenge Awards were instituted in 1995 to accord due recognition to the outstanding achievements in applied Green chemistry/Technology, with the first award being presented to Barry M. Trost in 1996. Drawing examples from the projects that have either received or have been nominated for the prestigious Presidential Green chemistry Challenge Awards, a few real world cases, e.g. Barry Trost's concept of atom economy, synthesis of ibuprofen, CO_2 gas – a blowing agent and development of oxidant activators for H_2O_2 , have been presented in this article. Some other examples that have been cited as representatives were drawn from the UK, Japan and Germany. Although we are far behind, the scenario in India appears to be not totally dismal. Some work in the 'Green' direction, though not in a very articulated manner, has been going on in the country. A non-exhaustive account of the works in the country, including a few examples from the workplace of the authors, has been presented. An attempt has been made to draw due attention of the educational policymakers, so as to enable incorporation of Green chemistry into the curricula, in terms of both theory and practice, at different levels of education. The need for a consortium approach of a proactive interaction of academia, technocrats and policy-makers has been emphasized.

CHEMICAL processes are as old as time, and over the centuries chemists have been trying to understand natural processes to develop methods based on the philosophies that are nature's very own. However, there lies a difference in that, while nature when working on any synthesis adopts methods following routes that eliminate almost completely the use and generation of substances hazardous to human health and the environment, chemists/technologists do not seem to rank the environment

very high in their priorities. This is the reason why natural processes are 'green' while synthetic processes are often 'grey'. In fact, chemical technology has been rather malevolent in a number of cases. Some of the most infamous examples are: (a) DDT, an insecticide effective in controlling insect pests, was responsible for causing a precipitous decline in the bald eagle population and is a suspected carcinogen; (b) the Cuyahoga river in Ohio was so polluted that it actually caught fire; and (c) the chemical accident in Bhopal (India) in December 1984 that resulted in the deaths of several thousand people. The reason for this malevolence can be attributed to the fact that a number of commonly used chemicals have

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high levels of intrinsic toxicity, and these environmentally hostile chemicals often have their domains existing far beyond the laboratories in which they are prepared or handled. In fact, substantial damage to the environment seems to have resulted from the actions of chemists and chemical technologists in the 20th century, for many of them paid little attention to investigating, publicizing and protecting against the risks of the chemicals which they produced or used. This should have been done since neither chemistry nor chemical-based products can be abandoned, because they are essential. Just one example that suffices to justify the need for chemistry is that it has increased our life expectancy from 47 years in 1900 to 75 years in 1990 (ref. 2).

In recent times, with the environmental degradation beginning to take alarming proportions, there has been a global improvement in the environmental awareness. Consequent upon this, the environmental protection laws are gradually being made more and more stringent. Though several legislations have been made and many more are being formulated against the use of detrimental chemicals and pollutants, the implementation of rules alone is not expected to be an end in itself. It is equally necessary for all practising chemists/technologists to realize the importance of preservation of the environment. In fact, had researchers sought to investigate more benign routes for chemical synthesis decades ago, most of the environmental and health-related problems that owe their origin to chemical pollutants, would have been averted or reduced considerably.

Looking at the global scenario, it becomes apparent that while the present-day chemistry is driven by an unparalleled social demand for better products and services, there is also a growing sentiment that an undue exploitation of resources must be minimized. However, with preservation of the environment being a major concern, the chemical industry has to now seek to wean users away from the conventional methodologies by driving towards those that are more efficient and environmentally benign. In this there seems to be a dichotomous challenge as, on the one hand, there is a requirement for increasing synthetic efficiency in chemical transformations, while on the other, there is a demand for minimizing environmentally hostile wastes. And thus, there lies a responsibility on chemists and chemical technologists in the development of a more sustainable chemistry, rendering it incumbent upon them to promote and disseminate awareness of environmentally compatible synthetic pathways throughout the academic and industrial research community, thereby setting a scene for the emergence and growth of a concept which allows for improving the quality of life and environment.

Insofar as India is concerned, it is possible that some thinking may have been going on in the 'green' direction in our country, but we are not sure of any coordinated effort being made in a well-orchestrated manner. Hence it is imperative to take note of the prevailing situation because India is also an important global player in human resources production, even though it may stand way behind in terms of industrialization. Thus, the human resources need to be trained in a manner that keeps pace with the contemporary international requirements. It is with this intent that the authors have made an attempt to put their thoughts together, under the back-drop of certain measures that have been taken by some of the industrially developed nations. It would be rewarding if the readers take some time out to provide inputs to help set guidelines, in order to address the issue in a manner that is conducive to adaptation to the Indian context.

How to go by

It seems to be a thousand dollar question, but one of the more effective ways of implementation of the design and development of newer methodologies, chemicals and technologies would be better driven by the mandates based on the following considerations:

- (i) The knowledge of what is hazardous and what is innocuous, and an enhanced cost of handling and disposing of hazardous materials;
- (ii) An ability of chemists to manipulate molecules to achieve an absoluteness in target-oriented synthesis by way of getting only the desired substances, as far as possible;
- (iii) Call for replacement or modification of older processes by the methodologies and products that could reduce or eliminate the use and generation of hazardous substances; and
- (iv) Providing awareness leading to consciousness among people of all ages.

The advent of Green chemistry

It is a mission in search of a solution to the problem that some novel approaches have converged into a distinctive discipline with the strategic objectives being increased efficiency, sustainability, and finally, societal benefit. And this discipline is that of 'Clean chemistry', more commonly known as 'Green chemistry'.

What does Green chemistry define?

'By definition, Green chemistry is the design, development, and implementation of chemical products and processes to reduce or eliminate the use of substances hazardous to human health and the environment'3. Members of this relatively new field have been making pathbreaking efforts to reduce the evil consequences of the chemical industry. Their efforts are also to allow economic progress and environmental growth to proceed in harmony. This new branch of science that includes modi-

fication of engineering practices and bioremediation, also promotes catalytic processes and eco-friendly reaction media, as well as the concept of atom economy leading to almost zero waste.

Consequently, there have been efforts to achieve environmentally benign synthesis and various acts have been passed to control and treat pollution, in an endeavour to encourage industries and academics to devise novel technologies, processes and educational materials, discouraging the formation or use of hazardous substances. This revolution is rather recent and started in the real sense in the 1990s, especially in the developed nations like the US, Germany and UK, for instance. Eventually, it is appreciated that while it is necessary to proclaim enactments and legislations, what is perhaps more important is the realization of detriments not only by the chemists/technologists, the academia and policy makers but also by the common mass in good proportion, to enable create a sense of resistance.

Green chemistry awareness initiatives

Some developed nations have done quite well to realize the importance of the concept of Green chemistry. A few examples have been highlighted below to convey the seriousness with which those countries addressed this problem, finally leading to the implementation of the 'green' concepts in a good measure.

The Presidential Green chemistry challenge awards

USA has been a forerunner in the promotion of this awareness. Realizing that an incentive was also required in order to bring about a more effective implementation, there are awards given at the presidential level, pronounced as the Presidential Green Chemistry Challenge (PGCC) Awards, which are presented annually at the National Academy of Sciences in Washington DC to promote the design of chemical products and manufacturing processes that prevent pollution and are economically competitive. In fact, these are the only awards for chemistry that are given away at the presidential level. Five awards are distributed each year with the categories being: academic, small business, alternate synthesis, alternative solvents or reaction conditions, and designing safer chemicals.

It may be mentioned that some other countries, namely UK, Australia, Italy, have instituted several awards to render Green chemistry practice more popular and lucrative.

International and National Symposia and Meetings on Green chemistry

(i) The CHEMRAWN Committee was founded in 1975 to drive an initiative of the International Union of Pure

and Applied Chemistry (IUPAC) to help address some of mankind's most pressing problems. The Green chemistry theme of CHEMRAWN XIV, founded in 1997 in Geneva, builds on the efforts of the IUPAC Working Party on 'Synthetic pathways and processes in Green chemistry'. (ii) Equally encouraging has been the Gordon Conference on Green chemistry which was started in 1996 with the recent one in the series being held in 2000, while the next meeting is slated for September 2002. (iii) An International Symposium on Green chemistry was held in Swansea, Wales in April 2001, in an effort to broadening the scope of the coverage from chemistry to include Green Chemical Engineering and Technology, and Educational Issues by presentations from industries. (iv) IUPAC Symposium: The first IUPAC International Symposium on Green chemistry was conducted in New Delhi in 2001 with over 220 delegates, including 40 from abroad. Many excellent presentations during the conference illustrated the interdisciplinary nature of Green chemistry. (v) National Symposium: The first National Symposium on Green chemistry was held in 1999 at the University of Delhi, as a part of the Indian venture.

The American Chemical Society – Environmental Protection Agency Green chemistry Programme

The Green chemistry Programme, developed through collaborations with academia, industry and government agencies fosters research, development and implementation of innovative chemical technologies that prevent pollution in a scientifically sound and cost-effective manner. The Environmental Protection Agency (EPA) introduced Green chemistry as a formal focus area in 1991 and it works for the recognition and promotion of chemical technologies for the reduction or elimination of the use of hazardous substances during the design, manufacture and use of chemical products and processes. The American Chemical Society (ACS)-EPA proactive joint venture also took the responsibility of developing educational materials, including laboratory experiments for different levels of education. A very good initiative indeed!

Distinctly noticeable programmes initiated in some other countries

(i) An organization called Green & Sustainable Chemistry Network (GSCN) was established in Japan in 1999. (ii) The Green chemistry Network which was launched a couple of years ago by the Royal Society of Chemistry is aiming to promote awareness and facilitate education, training and practice of Green chemistry in industry, academia and schools.

Tenets of Green chemistry

An evaluation of how green a chemical reaction or a chemical process is, seems to be best done in terms of the 12 principles that have been advocated by Anastas and Warner (see refs 2 and 4). These tenets deal with fundamental issues such as pollution prevention, atom economization and toxicity reduction. The essence of the 12 principles may be summarized as follows:

Waste prevention instead of waste clean-up, atom economy as an important concern, design of environmentally friendly synthetic methodologies, design of safer chemicals, redundancy of auxiliary substances, conservation of energy, use of renewable feedstock, reduction of unnecessary derivatization, catalytic reactions instead of stoichiometric ones, debasement of final products after the end of their function, real-time analysis for pollution prevention and strategies for chemical accident prevention.

Typical real world cases

A few cases as country-wise representative examples are given below:

Examples from Japan

Case 1. TiO_2 photocatalysts in Green chemistry⁵: Second-generation titanium oxide-based photocatalytic systems have been developed and shown to be important for the purification of polluted water, the decomposition of offensive atmospheric odours as well as toxins, the fixation of CO_2 and the decomposition of chlorofluorocarbons on a huge global scale.

Case 2. Oxidation of sulfides to sulfoxides and sulfones with 30% hydrogen peroxide under organic solvent and halogen-free conditions⁶: R. Noyori, in continuation of his design of routes to greener synthesis using hydrogen peroxide^{7a-c}, reported that aromatic and aliphatic sulfides have been oxidized to sulfoxides or sulfones in high yield with 30% hydrogen peroxide under organic solvent and halogen-free conditions. Dialkyl and alkyl aryl sulfides were cleanly oxidized to sulfoxides using aqueous hydrogen peroxide without catalysts. The best catalysts for the sulfone synthesis consist of sodium tungstate, phenylphosphonic acid and methyltrioctylammonium hydrogen sulfate. It is notable that primary or secondary alcohol or olefin moieties were unaffected under the conditions studied.

Case 3. Solvent-free organic reactions: Equally significant are the solvent-free organic reactions as pioneered by Toda and his coworkers^{7d,e}. It has been demonstrated that a variety of reactions falling under the following

general categories can be very successfully achieved without the intervention of a solvent. The different types of transformations include: oxidation, reduction, addition, elimination, C–C coupling reactions, substitution reactions, aminolysis, hydrolysis and transesterification reactions, polymerization, and rearrangement and isomerization reactions. It is believed that solvent-free organic synthesis and transformations are industrially useful and largely green.

Examples from Germany

Case 1. Oxidation reactions in the synthesis of fine and intermediate chemicals using environmentally benign oxidants and the right reactor system8: Environmentally benign oxidants such as molecular oxygen, hydrogen peroxide or nitrous oxide, showing high selectivity towards the desired oxygenated products can be activated on suitable heterogeneous catalysts, for the synthesis of fine and intermediate chemicals. Several examples illustrate that some features known from the synthesis of bulk chemicals can successfully be applied for manufacturing intermediate and speciality chemicals applying conventional industrial reactor systems. Direct oxidation of isoprenol, \(\beta\)-picoline and benzene are chosen as examples for continuous gas-phase processes, and oxidation of pinene and propylene are examples for semi-continuous or batch-wise processes in the liquid phase.

Examples from UK

Case 1. Environmentally friendly catalysis using supported reagents: the fast and selective bromination of aromatic substrates using supported zinc bromide^{9a}: Acid-activated montmorillonite (K-10) or mesoporous silica (100 Å) is used as a fast, selective catalyst for the para-bromination of activated and mildly activated aromatic substrates (Scheme 1). The system allows harmful chlorinated solvents to be replaced by less damaging hydrocarbon solvents. It is relevant to mention that a similar bromination by Br_2 absorbed on alumina was reported by Ranu et al.^{9b}.

Case 2. The new Upjohn route to hydroquinone¹⁰: Hydroquinone is a very useful intermediate in the manufacture

Scheme 1.

Scheme 2.

$$H_3C$$
 — CH + CO + H_3C — CH — CH

100 % atom economy **Scheme 3.**

of polymeric materials. The classical route suffers from very poor atom utilization and also leads to the production of enormous volumes of waste (Scheme 2). The new Upjohn route is a great improvement in that only 3 kg of acetone waste is produced per 10 kg of hydroquinone produced, and there are no significant amounts of salt waste.

Examples from USA

Case 1. The concept of atom economy¹¹ and the synthesis of methylmethacrylate¹²: Among the progenitors of Green chemistry is Stanford Chemistry Professor Barry Trost, who first proposed the concept of 'atom economy' in 1973 (ref. 11). The synthesis of methylmethacrylate¹² is taken as an example to describe the concept of atom economy (Scheme 3).

Rather than judging a chemical process successful if it produces usable product at a satisfactory cost, Trost argued that those responsible for synthesizing chemicals

Scheme 4.

$$H_3C$$
 C_gH_{11}
 H_2O_2
 C_gH_{11}
 C_gH_{11}

Scheme 5.

should aim for elegant efficiency for using the highest possible percentage of input atoms in the usable output, ideally leaving zero waste. This seemed a utopian concept when first proposed, but an increasing number of bio-catalytic and other chemical processes are now being proposed that achieve exactly such an outcome.

Case 2. Enzyme catalysis. Preparation of adipic acid from glucose using genetically altered E. coli: Enzyme catalysis in chemical transformations is expected to play an important part in practising Green chemistry. The preparation of adipic acid from glucose requires the conversion of glucose to cis, cis-muconic acid first. This apparently involves more than one step which is enzyme catalysed, as shown in Scheme 4.

Case 3. Iron-catalysed olefin oxidation¹³: By emulating natural oxidations by certain enzymes that have iron at their active sites, two research groups^{14,15} have very recently made significant progress towards environmentally friendly reactions that oxidize organic compounds using relatively nontoxic metal catalysts. The catalyst ligands used with the iron are inexpensive and simple to make, unlike the complex porphyrin ligands called hemes that are found in some enzymes. And the new reactions use hydrogen peroxide as the oxidizing agent, which results in harmless water as the by-product (Scheme 5).

Some cases of Green chemistry/Technology that have won the Presidential Green chemistry Challenge Awards may be cited as ideal examples:

- □ Barry Trost's *concept of atom economy*, which looks at utilized and wasted atoms in a reaction.
- □ Development of *surfactants for carbon dioxide*, enabling CO₂ to be used as a solvent (for example in dry cleaning).
- □ Development of *oxidant activators for hydrogen per-oxide*. This allows, for example, the replacement of chlorine-containing (ozone-depleting) bleaches with hydrogen peroxide in the manufacture of paper.
- □ A new *synthesis of ibuprofen* which has a much better record of atom economy and pollution prevention¹²: 4-isobutylacetophenone is a key intermediate in the manufacture of the bulk active pharmaceutical, ibuprofen. The conventional method of preparation is based on a protocol that uses a toxic chemical, i.e. aluminium chloride in stoichiometric amount, which results in enormous amount of aluminium trichloride hydrate as a waste by-product that is landfilled. Boots, in collaboration with Hoechst Celanese, developed a new cleaner process (Scheme 6).
- □ The use of waste carbon dioxide as a blowing agent (which is nonozone-depleting, unlike the traditional CFC blowing agents) for polystyrene foam (PS)¹². Carbon dioxide can be used as an environmentally friendly blowing agent for PS foam (Figure 1). According to reports, 6.6 billion pounds of PS are produced per year. Traditional methods used CFCs as blowing agents. CFCs are ozone-depleters and production was halted in 1995 in USA.
- ☐ The development of *new insecticides* that are more specific to target organisms.
- ☐ Greener gasoline alkylation¹⁶: Isooctane constitutes an integral part of gasoline. The conventional method of synthesis of isooctane requires large amounts of highly toxic and corrosive acids. The greener alternative is the use of suitable solid acids such as alumina, zeolites or Nafion polymer (perfluoropolymer with -SO₃ side group).

$$CH_{3} \xrightarrow{CH_{3}} H + \frac{S \text{ olid A cld}}{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3}$$

Examples from India

India, as we understand, though well on its way, has not possibly metamorphosed into a reckonable environmentally conscious nation in the strict sense and the relevance of Green chemistry figures somewhat low down in the agenda than the position it deserves. It seems that in an industrially and technologically developing country, the question of 'grey' or 'green' may not mean much.

Scheme 6.

However, it is also a fact that in relatively more industrialized areas, there has been a substantial increase in the air, water and soil pollution levels due to the unscrupulous use of toxic chemicals. With industrialization being the cause of pollution, it would seem that industrialization and pollution are concurrent, but the latter is not unmanageable if it is articulated properly. It is to be reiterated that the environment needs to be protected from chemical pollution and it is hoped that there shall be an eventual possibility of inculcating Green chemistry/ Technology culture in our country, by taking appropriate measures at the right time.

In fact, insofar as the practice of Green chemistry is concerned, there have been some activities in several research groups in our country. In order to highlight India's participation in a matter of global concern, a few cases that could be readily accessed by the authors have been cited. This should in *no way be mistaken for a comprehensive listing*. A few examples in support of our contention are set out below:

Case 1: Development of solid support reagents and catalysts useful for organic transformations: 'Clayan', Mg-Al-O-Bu'-hydrotalcite¹⁸, montmorillonites¹⁹, and a layered double hydroxide fluoride-solid base catalyst for C-C bond formation²⁰ provide a few examples of the solid support reagents that have been developed at IICT, Hyderabad (Scheme 7).

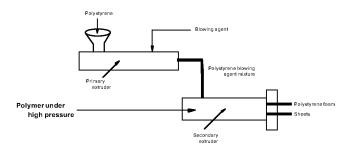


Figure 1. Production of polystyrene foam.

These are used for a variety of reactions such as deprotection, oxidation, oxidative coupling, nitration and bromination of activated and deactivated arenes, for cyanoethylation of alcohols and thiols, for selective synthesis of β -nitroalkanols, and for acylation of alcohols with carboxylic acids. It may be commented that the use of CH₂Cl₂ as a solvent is not ideal, as chlorinated solvents are quite high on the list of toxic solvents, and a greener solvent would be preferable. However, the ability to use one of the most ideal catalysts is a significant move in the right direction.

Case 2: While working on the reactivity of peroxometal compounds²¹, especially oxidation of halides, attention was drawn to the commercial importance of bromoorganics. Because of the use of brominated organic molecules as precursors for the preparation of pharmaceuticals, agrochemicals, speciality chemicals and so on²², these compounds have assumed high importance in contemporary chemical technology scenario. The bromoorganics, particularly bromoaromatics, are generally prepared involving toxic chemicals, for instance Br2, which has been a cause of great concern globally. Keeping environmental safety in sight, one would like to bypass the routes involving such chemicals, without sacrificing the goal of obtaining the target molecules with acceptable yield and cost. Indeed, it has been possible to develop newer and ecofriendly bromination protocols and brominating agents²³. These reagents and protocols have been gaining remarkable popularity²⁴. Candidly, this has been the turning point for the group insofar as Green chemistry practice is concerned. Our endeavour, in conjunction with the knowledge gained from the literature 10,25, has guided us to appreciate the importance of practising Green chemistry (Scheme 8).

In a rather recent endeavour, an experiment has been developed to demonstrate 100% atom economy in the synthesis of pyridinium fluorochromate (PFC), $C_5H_5NHCrO_3F$ (Scheme 9; unpublished results).

3 Bu₄NHBr₃ + H₂O₂

Bu₄NBr₃ + 2 Bu₄NOH

Ar-H + Bu₄NBr₃

Ar-Br + Bu₄NBr + HBr

$$+ Bu_4NBr_3 + Br + Bu_4NBr + Br$$

R + Bu₄NBr₃

OAB

$$V_2O_5 \text{ or } H_2MnO_4.H_2O/H + HO_3.KBr \text{ or } NH_4Br$$

Organicammonium Tribromide (OATB)

The earlier method of preparation involved Br₂ and HBr

$$Bu_4NBr_3 + ROH$$
 $ROH + O$
 R

Scheme 8.

% Atom economy = (MW of atoms utilized/MW of all reactants used in the reaction) \times 100, % Yield = (Actual yield of product/theoretical yield of product) \times 100.

Importantly, this reaction has been shown to work in a literally stoichiometric manner with the experimentally obtained yield being 97-99%, without requiring any external heating. This has been a practice experiment for graduate students to demonstrate Barry Trost's atom economy principle. The reaction can be scaled up to a kg level, if desired. It is noteworthy that PFC, an indigenous reagent, has served as one of the most useful oxidants for partial oxidations and selective oxidations²⁶ of a variety of organic substrates. Significantly, the partial oxidation of organic molecules, particularly hydrocarbons, is a widely used and multifarious area of chemistry having applications in almost all of the important fine and speciality chemicals industries manufacturing pharmaceuticals, agrochemical and monomers. Most of these processes use stoichiometric reagents. Interestingly, among the stoichiometric metal oxidants, chromium(VI) perhaps is the best known oxidizing agent in chemistry though its use on a large scale gives rise to a large volume of a toxic metal waste. Rather astonishingly, Cr(VI) reagents still continue to be used in many industrial processes such as the transformations of secondary alcohol functions to ketones generating larger volumes of waste than product, at times, in the process. But high added value of partially oxidized products will continue to render the chemistry economically more viable, though it may not be considered environmentally very favourable. However, a silver lining in the cloud is that the chromium waste can be collected or trapped depending upon the volume, and then land-filled.

Fortuitously though, some other syntheses developed by this group several years ago also seem to qualify to be ecofriendly processes, e.g.

$$Fe(OH)_3 + 3 acacH \rightarrow [Fe(acac)_3] + 3H_2O$$
,

$$[Ni^{III}O(OH)] + 3 acacH \rightarrow [Ni(acac)_2] + 1/2('acac-acac') + 2H_2O.$$

Metal acetylacetonates are extremely useful compounds, being used both in bench-scale as well as industrial-scale operations²⁷.

With a sustained effort, it has been possible to imbibe, at least in part, a Green chemistry culture in the workplace of the authors leading to the emergence of more than one group to participate in the practice of the tenets of Green chemistry. Some examples of the work done to this end include preparation of aurones and flavones ^{24c}, tetrabutylammonium tribromide (TBATB)-promoted tetrahydro-pyranylation/depyranylation of alcohols ^{24b}, cleavage of *tert*-butyldimethylsilyl (TBDMS) ethers ^{24d} and oxidative esterification of aldehydes ^{24f} (Scheme 10).

Case 3: Realizing the toxic effect of many volatile organic solvents, particularly chlorinated hydrocarbons, a

Scheme 10.

research group at IACS, Kolkata initiated a programme to develop green synthetic methods by designing reaction protocols without involving organic solvents. Noticeable success has been achieved by this group of workers by carrying out several useful transformations under the following 'safer' conditions²⁸: (a) Reactions on solid surface of benign solid inorganic support without solvent; (b) Reactions in aqueous media; (c) Reactions in ionic solvents, and (d) Reactions in neat without solvent.

Case 4: Also noteworthy are Kidwai's dry media reactions²⁹ used for the preparation of heterocycles, as a step towards Green chemistry.

Unfortunately, there appears to be a built-in dichotomy in our system. For instance, there are legislations setting acceptable limits on emissions, although not so strict regulations seem to be imposed to put a clear check onto the cumulative effects of chemicals on the environment. Hence, the problem is really not eliminated, but perpetuated. This looks rather like a half-baked cake! If we are to ensure the longevity of a clean environment, the porosity of the system should first be clogged. Thus, without speaking in too many words, the mandate is very clear, if we do not pretend to be ignorant.

Prospects

Back home, the chance of success in the domain of Green chemistry is surely not grim. But, the question is where to make a beginning and how to go about? While searching for an answer, we were reminded of a statement of Daryle Busch (former ACS President) 'Green chemistry represents the pillars that hold up our sustainable future. It is imperative to teach the value of Green chemistry to tomorrow's chemists.'30 Thus, it is quite indicative that the Green chemistry education material must be prepared for different levels of education in our country, the topics relevant to a level must be incorporated in the curriculum and the same must be implemented by providing essential teaching materials. This is expected to bring about a 'think green' culture at an early stage of learning. The lessons in words and examples in writing should be backed up by illustrative experiments that are already designed and tested well for this purpose. The EPA-ACS Green chemistry Educational Materials Development Project might serve as a reference. However, the material required in the 'Indian' context should be designed to suit the targeted audience. An interdisciplinary Science and Technology course on Green chemistry may be included at the graduate level for both science and engineering students.

At the level of research, Green chemistry and the related projects may be especially encouraged and appropriately funded. Attention may be drawn onto the possibility of establishing Green chemistry centres/facilities in a few

identified places. In case such thoughts are in the affirmative, the benefit accrued out of the investment made by the government should be made public for general awareness. This might make a positive impact on others as well. It may not be out of place to state, without meaning to be critical, that the policy makers might like to take appropriate measures in order to tighten the threads wherever they are loose. In a nutshell, it appears to be a collective responsibility of academia, technocrats and policy makers to make the venture successful. In other words, there should be a consortium approach to the whole issue.

Concluding remarks

While Green chemistry offers principles for the development of 'greener' reagents and alternatives and more benign routes to synthetic methodologies, it does not have the capacity to bring about a radical change. A consensus has to be arrived at between the policy makers and the chemical practitioners in order to give Green chemistry the power it rightly deserves. And a doctrine needs to be framed to guide the practitioners so that overall efficiency as well as environmental cleanliness are achieved. It is reiterated that the espouses for Green chemistry must involve not only the academia or academic intelligentsia but also the science and technology agencies and the S&T administrators, since it is only a synchronized movement of these apparently segregated entities that can bring about a reform movement in chemistry and chemical technology.

The role of the academia is to bring about a mass realization about the pertinence of Green chemistry. This body must also take upon itself to device appropriate educational material for different levels of curricular instructions. The research and development and the science and technology agencies that are responsible for the funding of scientific activities in the country must encourage and give preference to the development of greener science and technology. In order to ensure global environmental protection while keeping scientific and economic development on the forefront, the policy makers should understand the role of 'green' science and technology and make pollution prevention, rather than pollution control, their motto.

Though it is true that many industries and research organizations are yet to implement the principles of Green chemistry, nevertheless some of them have begun to realize that the 'think green' culture is more than just a fashion. In fact, the winds of changes have already started blowing and the more successful chemistry researchers and chemical technologists will like to appreciate and apply the values of Green chemistry in innovation, application and teaching.

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ACKNOWLEDGEMENT. U.B. thanks CSIR, New Delhi and S.K.D. thanks IIT, Guwahati for research fellowships.

Received 4 March 2002; revised accepted 6 May 2002

REVIEW ARTICLE

Plantations as a tool for mine spoil restoration

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Because of large-scale destruction of natural areas due to mining operations, a restoration strategy is needed as a part of the overall mining management plan. In restoration, emphasis is given first to build soil organic matter, nutrients and vegetation cover to accelerate natural recovery process. Tree plantations can be used as a tool for mine spoil restoration as they have ability to restore soil fertility and ameliorate microclimatic conditions. We discuss here various approaches of ecosystem restoration on mine spoil, criteria for the selection of plantation species and future research needs in this regard.

VAST areas of land all over the world have been rendered unproductive by human activities¹. The situation is particularly alarming in tropical areas where forest loss and degradation, as well as degradation of land that earlier supported forest, are proceeding at unprecedented rates^{2,3}. Ecosystem destruction by mining for coal, quarrying for minerals, and other processes to meet demands of industries, is an inevitable part of civilization⁴. The increasing human need for these resources will certainly accelerate further degradation of natural habitats, as most of the mining areas are on the land which was previously

occupied by forests. All these will lead to acceleration of erosion of biological diversity and creation of several other environmental problems.

The mine environment

As a result of mining and coal combustion, significant areas of land are degraded and existing ecosystems are replaced by undesirable waste materials in the form of dumps, tailing dams and ash dams⁵. The mineral extraction process drastically alters the physical and biological nature of a mined area. Strip-mining, commonly practiced to recover coal reserves, destroys vegetation, causes extensive soil damage and destruction and alters microbial communities⁶. In the process of removing desired mineral material, the original vegetation is inevitably destroyed and soil is lost or buried by waste⁷. We are usually confronted with a complete absence of soil, in either a pedological or a biological sense, and what is left is just a skeleton full of limiting factors⁴. Strip-mining can cause compaction, changes in soil texture⁸, loss of soil structure⁹ and reduced water infiltration. In addition, steep-sided soil piles are prone to erosion⁸.

Establishment of vegetation on abandoned mined lands is hindered by physical factors such as high temperature,

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