Implausible GCT: An Overview on its Role for Unscathed Environment in Modern Era

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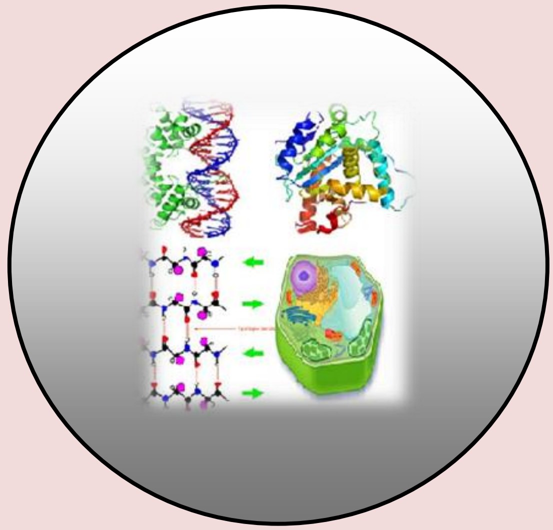
ISSN 2319-3077 Online/Electronic
ISSN 0970-4973 Print

Index Copernicus International Value
IC Value of Journal 82.43 Poland, Europe (2016)
Journal Impact Factor: 4.275
Global Impact factor of Journal: 0.876
Scientific Journals Impact Factor: 3.285
InfoBase Impact Factor: 3.66

J. Biol. Chem. Research
Volume 38 (2), 2021 Pages No. 155-193



Journal of Biological and Chemical Research

An International Peer Reviewed / Referred Journal of Life Sciences and Chemistry

Indexed, Abstracted and Cited in various International and National Scientific Databases

Published by Society for Advancement of Sciences®

J. Biol. Chem. Research. Vol. 38, No 2, 155-193, 2021
(An International Peer Reviewed / Refereed Journal of
Life Sciences and Chemistry)
Ms 38/02/7980/2021

ISSN 2319-3077 (Online/Electronic)
ISSN 0970-4973 (Print)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REVIEW ARTICLE

Received: 20/08/2021 Revised: 30/10/2021 Accepted: 30/10/2021

Implausible GCT: An Overview on its Role for Unscathed Environment in Modern Era

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ABSTRACT

The environment is a common resource shared by the entire globe. The impact of cumulative changes brought about by human activities is increasingly becoming evident both in terms of development and more so in the form of deterioration of the environment. Chemistry plays a pivotal role in determining the quality of modern life. The chemicals industry and other related industries supply us with a huge variety of essential products, from plastics to pharmaceuticals. However, these industries have the potential to seriously damage our environment, and hence there is a growing demand from society for a reduced reliance on fossil fuels and for greener manufacturing processes, as well as for future innovations to be built on more sustainable foundations. Green chemistry therefore serves to promote the design and efficient use of environmentally benign chemicals and chemical processes. Green chemistry, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances. Whereas environmental chemistry is the chemistry of the natural environment, and of pollutant chemicals in nature, green chemistry seeks to reduce and prevent pollution at its source. As a chemical philosophy, green chemistry applies to organic chemistry, inorganic chemistry, biochemistry, analytical chemistry, and even physical chemistry.

While green chemistry seems to focus on industrial applications, it does apply to any chemistry choice. Bioengineering is also seen as a promising technique for achieving green chemistry goals. Green chemistry consists of chemicals and chemical processes designed to reduce or eliminate negative environmental impacts. The use and production of these chemicals may involve reduced waste products, non-toxic components and improved efficiency. Green chemistry is a highly effective approach in pollution prevention because it applies innovative scientific solutions to real-world environmental situations. Chemical products and processes should be designed to the highest level of this hierarchy and be cost-competitive in the market. Green chemistry is a welcome step towards protecting the mother earth from ecological imbalance and environmental degradation posed by resource exploitation, urbanization, industrialization and bad agricultural practices incurred due to excess human activities. The term 'Green Chemistry' has emerged with an aim to protect human health and the environment in an economically viable and sustainable manner. 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. Green chemistry revolution provides an enormous number of opportunities to discover and apply new synthetic approaches using alternatives feedstock; eco-friendly reaction conditions, energy minimizations 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 sustainable world. One important element of green chemistry is commonly defined as the chemical research aiming at the optimization of chemical and products with respect to energy and material consumption, inherent safety, toxicity, environmental degradability, and so on. While considerable progress has 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 not different from traditional chemistry in as much as it embraces the same creativity and innovation that 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 consciousness throughout the world there is a change for chemists to develop new products, processes and services that achieve necessary social, economical and environmental objectives. This article delineates an assortment of day to day and industrial applications along with brief description on perspectives of GCT (Green Chemical Technology).
***Keywords:** Environmental degradation; Benign solvents; Safer chemicals; Bioengineering; Sustainability; Solid phase organic synthesis; Microwave; Ultrasound; Hazardous substances; E-factor and Atom economy.*

INTRODUCTION

Chemistry, sustainability and innovation—three key components are for the future of our society. Chemistry is an essential tool in our campaign to protect and preserve our environment, biodiversity and natural resources against further degradation.

It is also a primary driver both for the growth and sustainable development of the world economy and the well-being and quality of life of its citizens. The challenges for the chemical sciences are the key to solve the challenges that society will face over the next years: energy, food, clean water, medicines and vaccines, protection of our environment and cultural heritage, and economic development. [Ahluwalia and Kidwai, 2004, Anastas and Horváth, 2007, Anastas and Warner, 1998] At present, protection of the environment is a huge concern for society. Problems including global warming and ozone depletion highlight the negative effects human activity has on the planet. Not only the environment is getting affected by human endeavors but this also has detrimental effects on human health. Sustainable chemistry is therefore not only concerned with the reduction of hazardous substances and waste and the environmental impact of the chemical industry; it is part of a strategic long-term vision for the future of society, not disjoint from or antagonist to economic development but rather a key factor for innovation and competitiveness. In the current era there is a serious push towards developing processes that are eco-friendly. This necessitates a shift from the traditional concepts of the process efficiency that focuses exclusively on the chemical yield to one that assigns economic value to eliminating waste and avoiding the use of toxic and hazardous substances and focusing on more environmentally acceptable processes. To keep the green chemistry concern in mind, many industries are trying to synthesize target compounds by green chemistry routes. Chemistry has to and will play a major role to provide solutions for the crucial problems of the next century such as Energy; Use of renewable resources; green Pharma and Health; and environmental sustainability. Prompt global action to solve the energy crisis is needed. Such an action should be incorporated in a more general strategy based on the consciousness that the Earth's resources are limited. We are urged to save energy and to use energy in more efficient ways, and we are also forced to find alternative energy sources as soon as possible. The answer to the energy problem confronting this planet deals in the chemist's currency [Bailey, 1998, Calderone and Santos, 2012].

As chemists, we can help by improving energy technologies and, hopefully, finding a scientific breakthrough capable of solving the energy problem at its root. The production of renewable chemicals is gaining attention over the past few years. The natural resources from which they can be derived in a sustainable way are most abundant in sugars, cellulose and hemicellulose. These highly functionalized molecules need to be de-functionalized in order to match the traditional feedstock for the chemical industry. A fundamentally different approach to chemistry thus becomes necessary, since the traditionally employed oil-based chemicals normally lack functionality. This new chemical toolbox needs to be designed to guarantee the demands of future generations at a reasonable price. Many low carbon technologies including wind turbines, electric cars and catalytic converters require precious metals or other metals in unprecedented quantities threatening their continued availability. These elements are being dispersed in the form of waste throughout our environment, making them costly and difficult to recover. This emphasizes the necessity for a new approach to metal capture and use, thus increasing the lifetime of our reserves. The Pharmaceutical industry is the most dynamic part of the chemical industry [Clark, 1995].

It is in the forefront for big changes towards "greener" feedstock, safer solvents, alternative processes and innovative ideas. All these changes will increase the environmental credentials of the pharmaceutical industry, but at the same time will cut down cost and materials for the manufacturing operations making a step in the right direction of sustainability. Encouraging innovation, while integrating green chemistry and engineering into drug discovery, development and manufacturing of new pharmaceuticals is one of the most important issues in the health and pharmaceutical sector. Modern day civilization is largely dependent on the chemical industry for its current standards as well as better standards of living – "better living through chemistry" [Clarke, 2005]. The past few decades have been an era of successful chemistry-developments in water treatment, waste disposal methodologies, agricultural pesticides, fungicides, polymers, detergents, petroleum additives and many more. While all these advancements have contributed to the improvement in our quality of life, they come with a price tag of 'pollution'. The manufacture, use and disposal of synthetic chemicals have taken a toll on human health and environment [Davoudi and Evans, 2005, Finney et al., 2012, Frosch and Gallopoulos, 1989, Guchhait et al., 2012]. Today, with the 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 pollution prevention alternatives. Researchers and engineers from both the chemical industry, and the academic world have made efforts to correct pollution problems by the ore extensive use of 'Green Chemistry' concepts i.e. development of methodologies and products that are environmentally friendly. As the name implies, the green chemistry movement aims to make mankind approach to chemicals, especially synthetic organic chemicals, environmentally 'benign' or 'sustainable'.

TWELVE PRINCIPLES OF GREEN CHEMISTRY

Paul Anastas, then of the United States Environmental Protection Agency (USEPA), and John C Warner developed 12 principles of green chemistry, which help to explain what the definition means in practice. The principles cover such concepts as:

- the design of processes to maximize the amount of raw material that ends up in the product;
- the use of safe, environment-benign substances, including solvents, whenever possible;
- the design of energy efficient processes;
- the best form of waste disposal: not to create it in the first place.

The concept of green chemistry a-k-a sustainable chemistry [-the use of chemical principles and methodologies for source reduction, the most effective form of pollution prevention and it satisfy the principle "Prevention is better than cure". It considers the entire cycle of chemical processes as an opportunity for design innovation. It compasses education, research, and commercial application across the entire supply chain for chemicals. Rather than regulatory restrictions for controlling hazards, green chemistry challenges innovators to design and utilize matter and energy in a way that increases performances and value while protecting human health and the environment through reduction or elimination of the use or generation of hazardous substances] was coined by Paul Anastas and he along with John C Warner (1998) enunciated 12 principles of green chemistry (Fig. 1) towards ideal synthetic methods to save natural resources [Hall et al., 1999, Heine, 2007, Kang and Gade, 2012, Kawahara et al., 2012, Kim et al., 2012, Koshikari et al., 2012, Lanari et al., 2012, Lebow, 2004, Lin et al., 2012, Nagaraj et al., 2012, Padiya et al., 2012, Rajagopal, 2000].

The twelve principles are:

1. It's better to prevent waste than to treat or clean up waste after it is formed.

It refers to "zero" waste technology i.e. the waste than to treat or clean up waste after it's formed.

2. *Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.*

The objective behind this principle is to minimize byproducts in chemical transformation and reaction sequences. In other words it deals with the maximum incorporation of the reactant molecules in to the final product which give rise to the concept of atom economy. Atom economy is a simple calculation of percentage of the atoms in the reactants actually ends up in the final product. It's defined as

% atom economy = [(Formula weight of the product) / Sum of formula weights of all the reactants] x 100

Good atom economy refers most of the atoms of reactants are incorporated in the desired products and only a small amount of unwanted byproducts are formed and hence lesser problems of waste disposal or waste treatment. Thus atom economy is a very useful tool to minimize the environmental pollution level for the welfare of mankind and other living organisms.

3. *Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.*

It emphasizes that the hazardous or toxic substances should be minimized as far as possible by modifying existing synthesis pathways or starting materials/ reagents or application of modern technological tools. If any hazardous waste is produces, the chemistry should be designed to nullify the effect of the same on living organism including human beings.

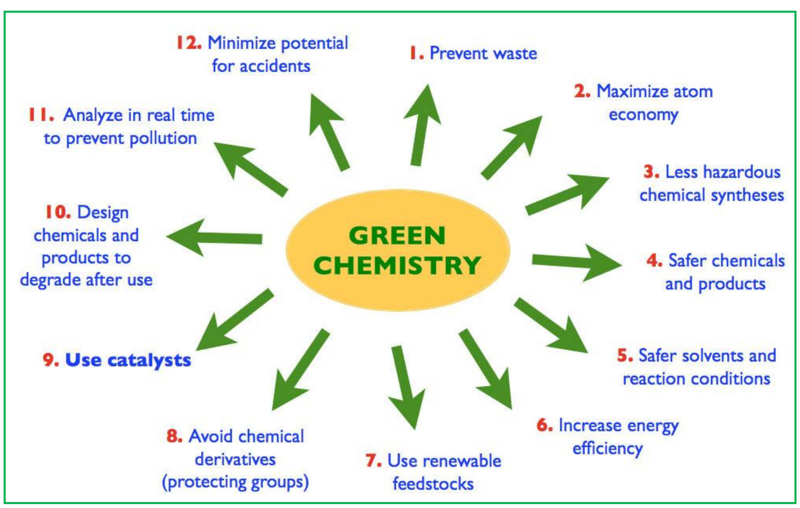


Figure 1. Twelve principles of green chemistry.

4. *Chemical products should be designed to preserve efficacy of function while reducing toxicity.*

In developing countries like India where workers are regularly exposed to chemicals during various steps of production processes, it's very much essential to define safer chemicals. Often not only the waste products but starting materials can also pose hazards. By way of manipulating the molecular structure, the toxicity of starting materials can be eliminated.

5. *The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.*

In many processing and manufacturing units (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used. In many processing and manufacturing units use of auxiliary substances in different steps can be avoided by exploring alternative methodologies or manipulations of auxiliary substances with water, so that the waste products will be less or non-toxic. If there is no option for using water as solvent, alternative methods may be developed for solvent fewer reactions.

6. *Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.*

This principles gives rise the concept of "green energy". It looks for the alternative ways to save energy or increase the energy efficiency of the system or produce energy from the waste products and use of the same for synthetic [processes. The energy demand for a synthetic process depends on various factors such as starting materials, solvent used and the reaction pathways; and manipulation of these factors may requires lesser energy than usual.

7. *A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.*

Overexploitation of non-renewable resources causes depletion of natural resources drastically giving rise to non-sustainability of resources. Sustainability means to ensure that future generation will have the opportunity to use their fair share of resources and will inherit a quality environment. Thus, more importance should be given on use of renewable resources than non-renewable. Use of renewable resources such as agricultural or biotechnology products are advantageous as it gives biodegradable process waste which generally not create any environmental problem.

8. *Reduce derivatives - Unnecessary derivatization (use of blocking group, protection/ deprotection, temporary modification of physical/chemical processes) should be avoided or minimized whenever possible as these steps require additional reagents and can generate wastes.*

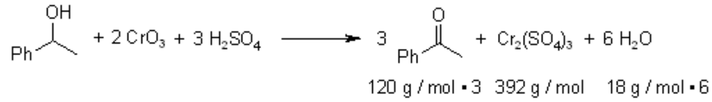
Especially in organic chemical synthesis, various blocking agents are used to get desired products which ultimately cause less atom economy and generation of more waste products which may be toxic. In some cases, salts or their derivatives are used to alter the physical properties like viscosity, surface tension, water solubility, etc. of the reactants to carry out desired processing. After completion of the reaction, these salts or their derivatives are obtained as product which would be a treat to the environment.

9. *Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.*
Catalysts provide alternative pathway to a reaction which makes the reaction faster and less energy consuming. It results 100% atom economy as catalysts are recoverable after completion of reaction without any alteration in its physical and chemical properties. Catalytic reaction also gives better results than synthetic reaction. Therefore, catalytic reactions are more preferable.
10. *Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.*
It depicts the waste product or by product from any chemical synthesis process should be biodegradable. Calcitrant or non-biodegradable moieties remain in environment for a longer period of time and cause detrimental effects on ecological systems. Sometimes the degradation product from biodegradable substances also possesses toxicity potential. So, proper investigation should also be carried out on toxicity of degradation products.
11. *Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.*
It deals with the analytical methodologies/protocols need to be developed or modified so that its efficiency/ accuracy gets increased. Continuous monitoring of the manufacturing and processing units is essential to make the industry premises free of any chemical mishaps.
12. *Substances and the form of a substance used in a chemical process should be chosen to minimize potential for chemical accidents, including releases, explosions, and fires*.
Substances, the gaseous reactant materials can become responsible for calamities in manufacturing/ processing plants as they are susceptible to explosion. Thus, the processing units must be designed to replace the gaseous materials with liquid or solid materials.
Implementing these Green Chemical Principles requires a certain investment, since the current, very inexpensive chemical processes must be redesigned. However, in times when certain raw materials become more expensive (e.g., as the availability of transition metals becomes limited) and also the costs for energy increase, such an investment should be paid back as the optimized processes become less expensive than the unoptimized ones. The development of greener procedures can therefore be seen as an investment for the future, which also helps to ensure that the production complies with possible upcoming future legal regulations. A typical chemical process generates products and wastes from raw materials such as substrates, solvents and reagents. If most of the reagents and the solvent can be recycled, the mass flow looks quite different:
Thus, the prevention of waste can be achieved if most of the reagent and solvents are recyclable. For example, catalysts and reagents such as acids and bases that bound to a solid phase can be filtered off, and can be regenerated (if require) and reused in a subsequent run. In the production of chemical products on very large scale, heterogeneous catalysts and reagent can be kept stationary while substrates are continuously added and pass through to yield a product that is continuously removed (for example distillation).
The mass efficiency of such processes can be judged by E-factor:

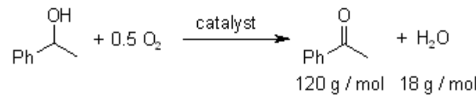
$$\text{E factor} = \frac{\text{Mass of wastes}}{\text{Mass of product}}$$

$$\text{atom efficiency} = \frac{\text{molecular weight of desired product}}{\text{molecular weight of all substances formed}}$$

examples:



$$\text{atom efficiency} = \frac{3 \cdot 120}{3 \cdot 120 + 392 + 6 \cdot 18} = 42\%$$



$$\text{atom efficiency} = \frac{120}{120 + 18} = 87\%$$

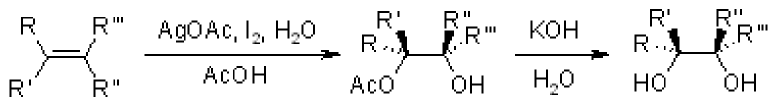
Whereas the ideal E-factor of 0 is almost achieved in petroleum refining, the production of bulk and fine chemicals gives E-factors of almost in between 1-50. Typical E factors for the production of pharmaceuticals lie between 25 and 100. It’s to be note that water isn’t considered in this calculation, because this world lead to very high E factors. However, inorganic and organic wastes that are diluted in the aqueous stream must be included. Sometimes it’s easier to calculate the E-factor from a different viewpoint, since accounting for the losses and exact waste stream is difficult.

$$\text{E factor} = \frac{\text{Mass of raw materials - Mass of product}}{\text{Mass of product}}$$

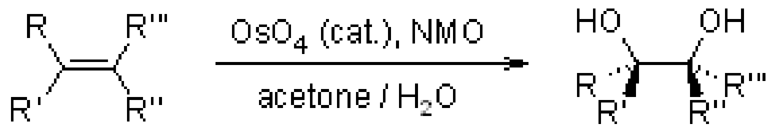
In any event, the E-factor and related factors don’t account any type of toxicity of the wastes. Such a correction factor (an “unfriendliness” quotient. Q would be 1if the waste has no impact on the environment, < 1 if the waste can be recycled or used for another product, and > 1 if the wastes are toxic and hazardous. Such discussions are at very preliminary stage, and E-factors can be used directly for comparison purposes as thismetric has been widely adopted in the industry.

Another attempt to calculate the efficiency of chemical reactions, also widely used, is that of atom economy or efficiency. Here the value can be calculated from the equation:

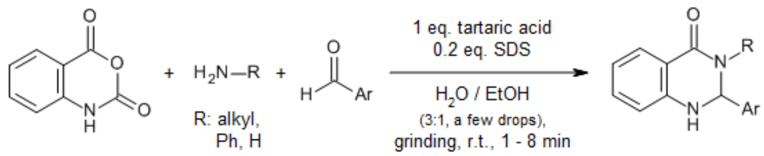
Atom efficiency is a highly theoretical value incorporating neither any solvent, nor the actual chemical yield. Experimental atom efficiency can be calculated by multiplying the chemical yield with the theoretical atom efficiency. Anyway, the discussion remains more qualitative than quantitative, and loss doesn’t yet quantify the type of toxicity of the products and reagent used. Still, atom economy as a term can readily be used for a direct quantitative description of reactions. Considering specific reactions, the development of green method is focused on two main aspects: choice of solvent, and the development of catalyzed reactions. By way of example, the development of catalyzed reactions for dihydroxylations have made possible the replacement of the *Woodward Reaction* in the manufacture of steroids, in which huge amounts of expensive Ag-salts were used and produced, and thus had become an economic factor:



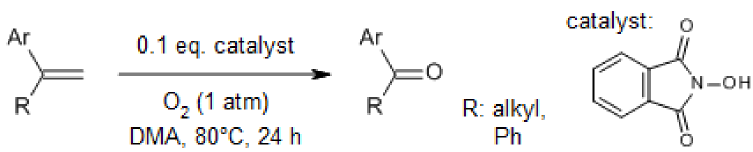
This reaction can be replaced through the use of stoichiometric quantities of OsO_4 which is both very toxic and very expensive, making its use on a commercial scale prohibitive. Only in its catalytic variant, which employs N-methylmorpholine-N-oxide as the stoichiometric oxidant and catalytic quantities of OsO_4, can be considered a green reaction that can be used on industrial scale.



Some systems have already been reported in which H_2O_2 is used to reoxidize the N-methylmorpholine-N-oxide allowing this material also to be used in catalytic amounts.
Considering the atom efficiency using H_2O_2 as the terminal oxidant, H_2O as the stoichiometric byproduct is much better than N-methylmorpholine. Notably, catalytic systems are available in which the Os catalyst is encapsulated in a polyurea matrix or bound to a resin, so that the catalyst can be more easily recovered and reused. An additional advantage of such polymer-bound catalysis is the avoidance of toxic transition metal impurities, e. g. in pharmaceutical products. A key point is still the choice of solvent, as this is the main component of a reaction system by volume (~90%), chlorinated solvents should be avoided, as many of these solvents are toxic and volatile, and are implicated in the destruction of ozone layer. Alternative solvents include ionic liquids, e. g., which are non-volatile and can provide non-aqueous reaction media of varying polarity. Ionic liquids have significant potential, e. g., since if systems can be developed in which the products can be removed by extraction or distillation and the catalyst remains in the ionic liquid, theoretically both the catalyst and the solvent can be used. The solvent for choice for green chemistry is water, which is non-toxic liquid and with limited chemical compatibility. On the other hand, reactions such as *Diels-Alder Reaction* are often even accelerated when run in an aqueous medium, while on the other hand, many reactants and reagents, including most organometallic compounds, are completely incompatible with water. There is great need to develop newer methods and technologies that would make interesting products available through reactions in water or other aqueous media. Chemical reactions run under neat conditions (no solvent) and in super critical CO_2 medium can also be considered as green choices. Other possible improvements can be considered, such as e. g., replacement of benzene by toluene (as a less toxic alternative), or use of solvents that can be rapidly degraded by microorganisms. It’s quite astonishing to consider the progress that has been made in the development of green alternatives to traditional reactions.

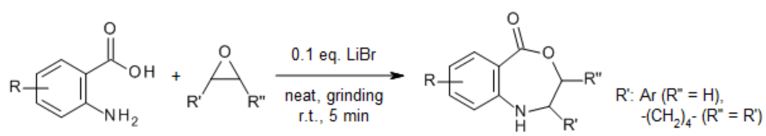


Utilizing a recyclable tartaric acid-SDS catalyst system help to achieve a green synthesis of 2,3-dihydro/spiroquinazolin-4 (1H)-ones via 3-component cyclocondensation reaction of isatoic anhydride, amines and aldehydes/ketones. Mechanochemical activation at r. t. lead to significant improvement on previously described methods for the synthesis of such compounds even in large-scale reactions[B].

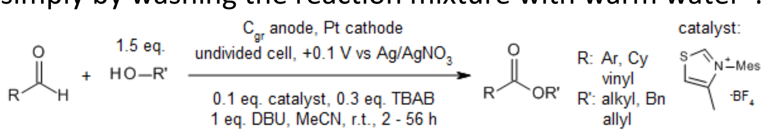


N-hydroxyphthalamide catalyzes a metal-free, aerobic oxidative cleavage of olefins.

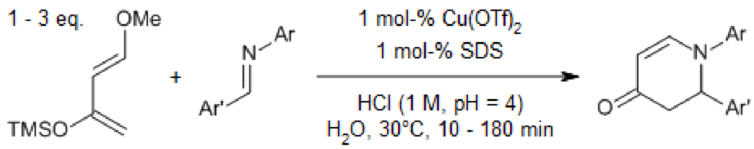
This methodology avoids the use of toxic metals or overstoichiometric amounts of traditional oxidants, showing good economic and environmental advantages. Based on the experimental observations, a plausible mechanism is proposed[C].



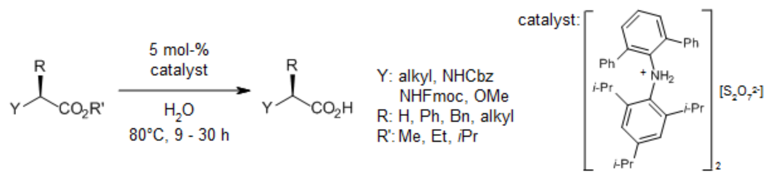
An atom-economic, efficient, rapid, and highly regioselective one-pot click reaction allows the synthesis of benzo[*e*][1,4]oxazepin-5-ones in excellent yields. The method involves epoxide ring-opening-ring-closing cascade with anthranilic acids using neat grinding at room temperature in the presence of lithium bromide as a mild catalyst. Pure products are obtained simply by washing the reaction mixture with warm water[D].



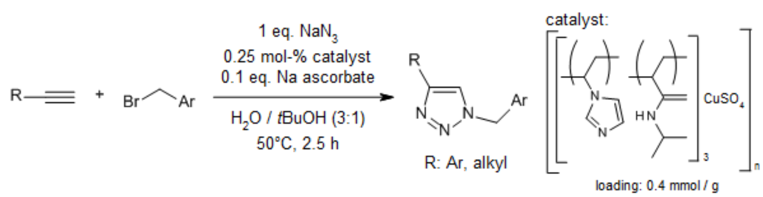
A one-pot conversion of aldehydes to esters interfaces N-heterocyclic carbene-based organocatalysis with electro-organic synthesis to achieve direct oxidation of catalytically generated electroactive intermediates. A broad range of aldehyde and alcohol substrates has been converted. Furthermore, the anodic oxidation reactions are very clean, producing only H_2 gas as a result of cathodic reduction[E].



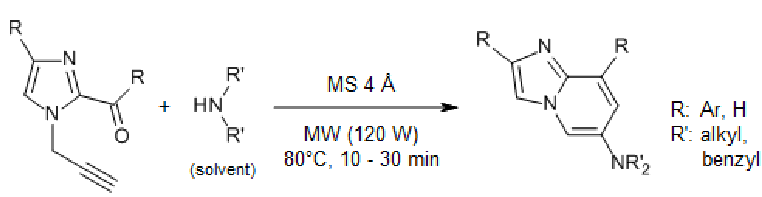
A reaction between *N*-benzylideneanilines and Danishefsky's diene proceeds smoothly in acidic aqueous medium in the presence of a catalytic amount of copper(II) triflate and sodium dodecyl sulfate to afford the corresponding 1,2-diphenyl-2,3-dihydro-4-pyridones in excellent yields. The aqueous solution containing the catalyst can be recovered and reused without any loss in efficiency[F].



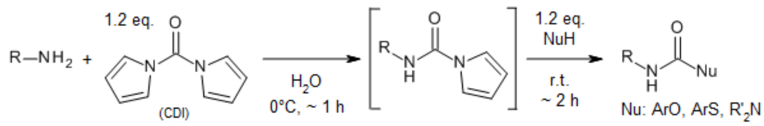
N,N-diarylammonium pyrosulfate efficiently catalyzes the hydrolysis of esters under organic solvent-free conditions. This reverse micelle-type method is successfully applied to the hydrolysis of various esters without the decomposition of base-sensitive moieties and without any loss of optical purity for α-heterosubstituted carboxylic acids[G].



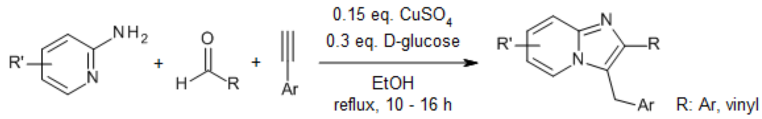
Self-assembly of copper sulfate and a poly(imidazole-acrylamide) amphiphile provides a highly active, reusable, globular, solid-phase catalyst for click chemistry. The insoluble amphiphilic polymeric imidazole Cu catalyst drove the cycloaddition of various of alkynes and organic azides at very low catalyst loadings and can be readily reused without loss of activity to give the corresponding triazoles quantitatively[H].



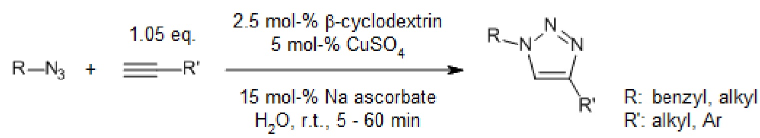
An efficient microwave-assisted metal-free amino benzannulation of aryl(4-aryl-1-(prop-2-ynyl)-1*H*-imidazol-2-yl)methanone with dialkylamines affords various 2,8-diaryl-6-aminoimidazo[1,2-*a*]pyridines in good yield[I].



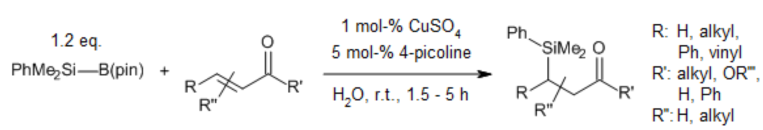
A one pot reaction of carbonylimidazolide in water with a nucleophile provides an efficient and general method for the preparation of urea, carbamates and thiocarbamates without an inert atmosphere. Products precipitate out from the reaction mixture and can be obtained in high purity by filtration[J].



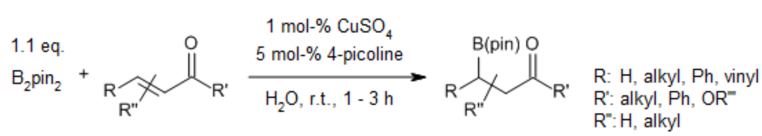
With a mixed Cu(I)-Cu(II) system in situ generated by partial reduction of $CuSO_4$ with glucose, an efficient and eco-friendly multicomponent cascade reaction of A^3-coupling of heterocyclic amidine with aldehyde and alkyne, 5-*exo-dig* cycloisomerization, and prototropic shift has afforded therapeutically important versatile *N*-fused imidazoles[K].



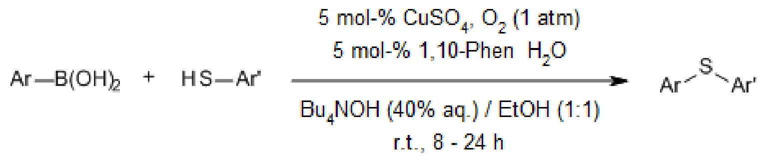
1,4-Disubstituted-1,2,3-triazoles were obtained in very good yields from azides and terminal alkynes in water in the presence of catalytic amount of β-cyclodextrin as a phase transfer catalyst. Also, one-pot reactions of alkyl bromides, sodium azide, and terminal alkynes were carried out successfully to give 1,4-disubstituted-1,2,3-triazoles[L].



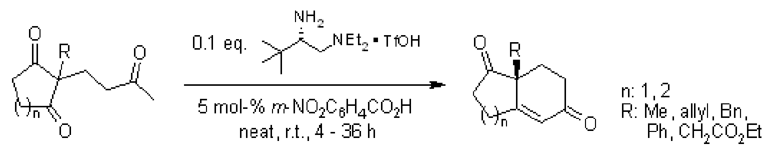
The presence of a catalytic amount of copper(II) and an amine base enables a mild method for the installation of the dimethylphenylsilyl group on the β-carbon of electron-deficient olefins at rt. The transformation proceeds efficiently in water within 1.5–5 h to afford β-silylated products in good yields[M].



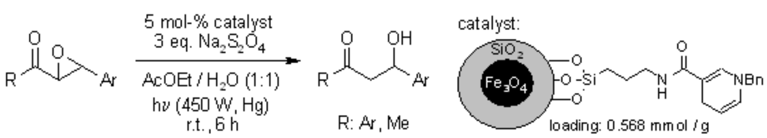
Using bis(pinacolato)diboron, catalytic amounts of Cu^{II}, and various amine bases in water under atmospheric conditions at rt, acyclic and cyclic α,β-unsaturated ketones and esters are β-borylated in good yield. Mechanistic investigations suggest that the role of the amine is not only to coordinate to Cu^{II}but also to activate a nucleophilic water molecule to form a reactive sp^2-sp^3 diboron complex[N].



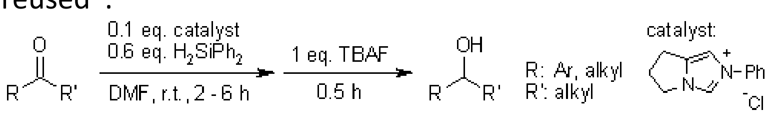
An efficient $CuSO_4$-catalyzed S-arylation of thiols with aryl and heteroaryl boronic acids at room temperature is established. A wide variety of thiols and arylboronic acids can be converted in the presence of $CuSO_4$ as the catalyst, inexpensive 1,10-phen·H_2O as the ligand, oxygen as oxidant, and EtOH as environment-friendly solvent[O].



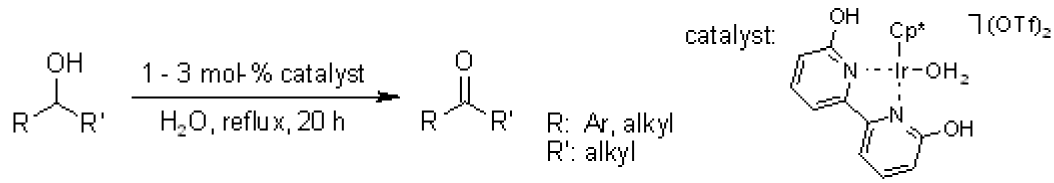
A simple chiral primary amine catalyses a highly efficient reaction for the synthesis of both Wieland-Miescher ketone and Hajos-Parrish ketone as well as their analogues in high enantioselectivity and excellent yields. This procedure represents one of the most efficient methods for the synthesis of these versatile chiral building blocks even in gram scale with 1 mol% catalyst loading[P].



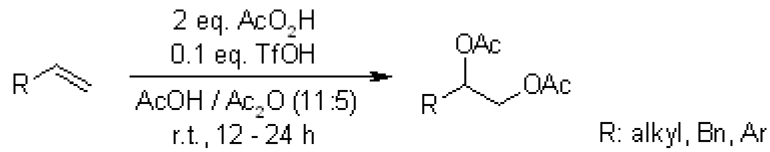
The of silica-coated magnetic nanoparticles allowed the construction of magnetically recoverable organic hydride compounds. Magnetic nanoparticle-supported BNAH (1-benzyl-1,4-dihydronicotinamide) showed efficient activity in the catalytic reduction of α,β-epoxy ketones. After reaction, the catalyst can be separated by simple magnetic separation and can be reused[Q].



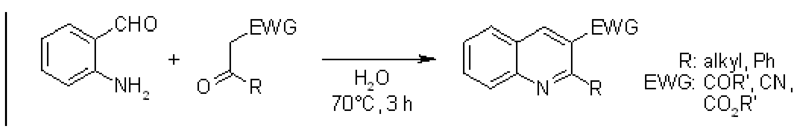
Activation of diphenylsilane in the presence of a catalytic amount of an N-heterocyclic carbene (NHC) enables hydrosilylation of carbonyl derivatives under mild conditions. Presumably, a hypervalent silicon intermediate featuring strong Lewis acid character allows dual activation of both the carbonyl moiety and the hydride at the silicon center. Some interesting selectivities have been encountered[R].



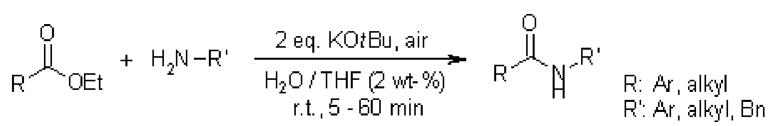
A water-soluble Cp*Ir complex bearing a bipyridine-based functional ligand can be used as catalyst for a dehydrogenative oxidation of various primary and secondary alcohols to aldehydes and ketones, respectively without any oxidant. The catalyst can be reused[S].



A clean and efficient and metal-free diacetoxylation reaction of alkenes using commercially available peroxyacids as the oxidants is catalyzed by triflic acid. This method enables also oxidative lactonizations of unsaturated carboxylic acids in good to high yields.



A straightforward and efficient method for the synthesis of quinolines via Friedländer reaction of 2-aminobenzaldehyde with various ketones or malononitrile can be conducted in water without using any catalyst at 70°C[T].



Aliphatic and/or aromatic esters were converted into the corresponding amides under mild conditions in good to excellent yields in the presence of t-butoxide, water and air. The reaction is highly efficient, rapid, versatile, green and economical, and could find great practical application in organic synthesis, biochemistry, and industrial chemistry[Q].

CURRENT ADVANCEMENTS IN GREEN CHEMISTRY APPROACHES

Normally microwaves have λ between 1mm and 1m (frequencies of 30GHz to 300 GHz). These are similar to frequencies of radar and telecommunication. In order to avoid any interference with these systems, the frequency of radiation that can be emitted by household and industrial microwave oven is regulated; most of appliances operate at a fixed frequency of 2.45GHz which is also preferred frequency viz. industrial, scientific, and medical applications as it has the right penetration depth to interact with the materials. [Ravichandran, 2010, Sato et al., 1998, Shen et al., 2012].

Microwaves are widely used in electron paramagnetic resonance spectroscopy (EPRS, communication, remote sensing, navigation, and food processing but in daily life, their well-established use is for heating and drying materials. It's nowadays utilized in almost household and industrial set up for this purpose. Microwave irradiation offers many advantages over conventional heating, such as non-contact, rapid and highly specific heating[Z1]. The mechanism of how energy is given to a substance which is subjected to microwave irradiation is complex. One view is that microwave reactions involve selective absorption of electromagnetic waves by polar molecules, non-polar molecules being inert to microwaves. When molecules with a permanent dipole are submitted to an electric field, they become aligned and as the field oscillates their orientation changes, this rapid reorientation produces intense internal heating. The main difference between classical heating and microwave heating, lies in core and homogeneous heating associated with microwaves, whereas classical heating is all about heat transfer by preheated molecules. The preferred reaction-vessel for microwave induced organic reaction, is a tall beaker (particularly for small scale reactions in the laboratory), loosely covered and the capacity of the beaker is maintained much greater than the volume of the reaction mixture. Alternatively, Teflon and polystyrene containers can be used. These materials are transparent to microwaves. Metallic containers use is avoided as reaction vessels (Shin et al., 2012).

In microwave induced organic reactions, the reactions are carried out in a solvent medium or on a solid support in lacking solvent. Choice of solvent is very crucial for reaction in solvent medium. The solvent used must have a dipole moment so as to absorb microwaves and a boiling point at least 20-30ºC higher than the desired reaction temperature. An excellent solvent is a domestic microwave oven is N, N-dimethylformamide (DMF) [bp=160ºC; dielectric constant (Ɛ)=36.7]. The solvent can retain water, thus, obviating the need for water separation. Some other solvents of choice are Foramamide [bp=216;11.1], methanol [65;32.7], ethanol [78;24.6], Chlorobenzene [214;5.6], 1,2-dichlorobenzene [180;1.53], 1,2,4-trichlorobenzene [214;1.57], 1,2-dichloroethane [83;10.39], ethylene glycol [196;37.7], dioxane [101;2.20], diglyme [162;7.0], triglyme [216;1.42]. Hydrocarbon solvents, e. g. hexane (Ɛ=1.9), benzene (Ɛ=2.3) and toluene (Ɛ=2.4) are unsuitable because less dipole moment and also because these solvents absorb microwave radiations poorly. However, addition of small amounts of alcohol or water to these solvents can lead to dramatic coupling effects. Liquids which don't posses dipole moment can't be heated by microwaves. By addition of a small amount of a dipolar liquid to a miscible non-dipolar liquid, uniform temperature under irradiation, is achieved.

Microwaves can be considered as a more efficient source of heating than conventional steam (or oil heated vessels), since the energy is directly imparted to the reaction medium rather than through the walls of a reaction vessel. In fact, the rapid heating capability of the microwaves leads to considerable saving in dissolution or the reaction time. The smaller volume of solvent required contribute to saving in cost and diminishes the waste disposal problemws[L3, L4]. Microwave procedures are limited[L5]. By the presence of solvents which reach their bps within a very short time (~1min) of exposure to microwave. Consequently, high pressures are developed, leading to damage to the vessel material or the microwave oven itself and can occasionally lead to explosion. Well-designed industrial microwave ovens are available now.

Considerations of the safety aspects coupled with the limitations of the solvents imposed by microwave heating, has led to many reactions carried out in water or more commonly under solvent free conditions. This is a major green advantage of microwave reactions. It's belied that due to high polarity and non-volatility, ionic liquids might be ideal foe carrying out high temperature reactions efficiently, since temperatures of over 200°C can be readily attainable. [Singh et al., 2012, Thorpe et al., 2012, Xu et al., 1997].

GREEN CHEMISTRY PRACTICES IN EVERYDAY DYNAMISM

With the advancement of science, green chemistry has changed our life style. Some of it important applications are described.

- **Dry Cleaning without PERC**

PERC ($Cl_2C=CCl_2$), commonly being used a solvent for dry cleaning. It is known that perc contaminates groundwater and is a suspected human carcinogen. A technology developed by Joseph De Simons, Timonthy Romack, and James Clain made use of liquid CO_2 and a surfactant for dry cleaning cloths, thereby replacing PERC. Dry cleaning machines have 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[2].

The dry cleaning industry, in particular, is highly dependent on solvents with ~ 100,000 drycleaners worldwide using perchloroethylene (perc) as the primary solvent. Numerous studies have shown pecr to be toxic, affecting plant workers and consumers who use drycleaners and people whose homes are in close proximity to dry cleaning establishments. Supercritical CO_2 has been developed and demonstrated as a viable alternative to perc in dry cleaning applications because it's environmentally friendly, non-toxic and biodegradable and requires no hazardous wastes removal, avoiding costly regulatory compliance issues. Furthermore, in 2003 Consumer Reports study CO_2 outperformed perc for dry cleaning applications. (www.consumerreports.org)

- **Versatile Bleaching Agent**

It is common knowledge that paper is manufactured from wood (which contains about 70% polyssacharides 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 NaOH and 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 Cl_2 gas. 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 (or aromatic substitution) to produce dioxins, such as 2, 3, 7, 8- tetrachlolo-p-dioxin and chlorinated furans. These compounds are potential carcinogen 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 H_2O_2, O_3 or O_2 also did not give the desired results. A versatile bleaching agent has been developed by Terrence Collins of Carnegie Mellon University.

It involves the use of H_2O_2 as a bleaching agents in the presence of some activators known as TAML activators[3] that act as catalyst which promote the conversion of H_2O into hydroxyl radicals that are involved in oxidation/bleaching. The catalytic activity of TAML allows H_2O_2 to breakdown more lignin in a shorter time and at much lower temperature, these bleaching agents also find use in laundry and result in lesser use of water[3].

- **Boat Based without Tin**

In 1998, Rohm & Haas Company received a PGCCA for designed the environmentally safe marine antifoulant called Sea-Nine™. Fouling, the unwanted growth of plants and animals on a ship's surface, costs the shipping industry ~ $3 billion a year. A significant portion of the cost is the increased fuel consumption need to overcome hydrodynamic drag. The main compounds used worldwide to control fouling are organotin antifoulants, such as trybutyltin oxide (TBTO). They are effective for preventing fouling, but have widespread environmental problems due to their persistence in the environment and they cause severe hazards, including acute toxicity, bioaccumulation, decreased reproductive viability, and increased shell thickness in shellfish. As a green alternative to TBTO, Rohm& Haas introduced a broad spectrum antifoulant based on isothiazolone chemistry. This product provides a long-lasting, stable formulation that is free of heavy metals and degrades rapidly when releases to the environment[Frey].

- **Fire Extinguishers without Foam**

The aqueous film-forming foams developed by the US Navy in the 1960s for use on volatile hydrocarbon fires release hydrofluoric acid and fluorocarbons during use, and the fluorosurfactants often lead to groundwater contamination. In 1993, PYROCOL technologies, Inc., developed more effective biodegradable, free from glycol ethers or fluorosurfactnts, fire extinguisher foam as a environmentally friendly alternative to current fire extinguisher agents.

- **Car Coating without Pb**

Pb (lead) has historically served as a necessary component in anti-corrosion coating, particularly in applications for automobile manufacturing and protection. But, Pb has been found to have long-term toxic effects in humans and natural systems. As an alternative to such coatings, the G industries developed a Pb-free cathodic epoxy e-coat for applications by automobile manufacturers. The innovative product is a waterborne coating with VOC and HAP concentration of < 0.5lb/gallon or 99% VOC and HAP free eliminating the resource expenditures associated with managing, monitoring and permitting these chemical classes. This new product reduces environmental impacts associated with the coating application (material transfer rates exceeding 98%) and eliminates the long-term use and exposure associated with Pb-based products[1++].

- **Lumber without Arsenic**

CCA is generally used for preservation of pressure treated wood. There are significant environmental implications associated with the production, use, storage, and disposal of these chemicals as well as potentially significant exposure of workers of these chemicals. Once these products are out of the marketplace, the major human health concerns are that daily contact with As leached from CCA-treated wood might lead to an increased risk for cancer or other long-term health implications.

One such alternative is Chemical Specialties, Inc. ACQ wood preservative. ACQ combines a bivalent Cu complex and a quaternary ammonium compound and offers equivalent performance against biological hazards, such as decay and termite attack to traditional formulations that contained as and Cr (VI).

- **MWFs without depleting Resources**

MWFs increase productivity and quantity of manufacturing operations by cooling and lubricating during metal forming and cutting processes. Despite their widespread use, they pose significant health and environmental hazards throughout their life cycle. MWFs are typically oil-in-water emulsions with both the oil and surfactant components being petroleum-based products. It also contains EDTA, a chelating agent and chemical of concern because once released to the environment it doesn't readily biodegradable and can remobilize heavy metals into food chain. An innovative MWF design has been proposed that uses bio-based oil and surfactants in the formulation and needs no EDTA. This new MWF formulation design provides better quality under anticipated field conditions and outperforms the current MWF products in terms of lubrication and wetting in actual manufacturing opertions.

- **Pest Control without Chemicals**

The estimated annual loss to growers from pests is $300 billion worldwide. In order to be successful, growers have generally pursued two approaches to limit economic losses and increase yield: use traditional chemical pesticides; or grow crops that are genetically engineered for pest resistance. Each approach has consequences including environmental effects that have come under increasing criticism from a variety of sources. In 2001, EDEN Bioscience Corporation received PGCCA for their product. Messenger®, a pesticide which is based on a new defense system to protect against proteins called harpins. Harpins triggers plant's natural defense system to protect against diseases cause by pests, and simultaneously active certain plant growth systems without altering the plant's DNA. When applied to crops, harpins increase plant biomass, photosynthesis, nutrient uptake, and root development, leading to greater crop yield and quantity. The use of harpins have been shown to have vitually no adverse effect on any of the organism tested, including mammals, birds, honey bees, fish, aquatic invertebrates, and algae. Harpins are fragile molecules that are degraded rapidly by UV light and natural microorganism; they have no potential to bioaccumulate or to contaminate surface- or groundwater resources. Spinosad is an environmentally safe pesticide but isn't stable in water and so therefore can't be used to control mosquito larvae. Clarke has developed a way to encapsulate spinosad in a plaster matrix, allowing it to be released slowly in water and provide effective control of mosquito larvae. The pesticide, Natural TM, replaces organophosphates and other traditional toxic pesticide and is approved for use in certified organic farming.

- **Ester Synthesis without using Toxic Acids and Solvent**

Esters are important ingredients in cosmetics and personal care products. Usually, thay are manufactured by harsh chemical methods that use strong acids and potentially hazardous solvents; these methods also require a great deal of energy.

Eastman's new method uses immobilized enzymes to make esters, saving energy and avoiding both strong acids and organic solvents. This method is so temperate that Eastman can use delicate, natural raw materials to make esters never before available.

- **Analyzer Tag Protein for Fast and Accurate Analysis Hazardous Chemicals or High Temperature**

Each year, laboratories test millions of samples of food for the presence of protein. Such tests generally use a large amount of hazardous substances and energy. CEM has developed a fast automated process that uses less toxic reagents and less energy. The new system can eliminate 5.5 million pounds of hazardous waste generated by traditional testing in the US each year. What's more, it differentiates between protein and other chemicals used to adulterate food, such as melamine.

- **Bio-based Toners**

Traditional toners of laser printers and copiers fuse so tightly to paper that they are difficult to remove from waste paper for recycling. They are also made from petroleum-based staring materials. Battelle and his copartner, AIR and the OSC, have developed a soy-based toner that performs as well as traditional ones, but is much easier to remove, the new toner technology can save significant amounts of energy and allow more paper fiber to be recycled.

- **Medical Sterilization without Ethylene-oxide or γ-Radiation**

Sterilizing biological tissue for transplant is critical to safety and success in medical treatment. Common existing sterilizing techniques use ethylene oxide or **γ**-radiation, which are toxic or posses heavy safety problems. NovaSterilis invented a technology that uses CO_2 and a form of peroxide to sterilize a wide variety of delicate biological materials such as graft tissue, vaccines, and biopolymers. Their Nova 2200™ sterilizer requires neither hazardous ethylene oxide nor **γ**-radiation.

- **Biofuel from Pulp Waste**

Pulp and paper industry is among the major sources of industrial pollution. But they could soon double as biorefineries. The Swedish company Chemrec has developed a process for turning the black liquor left over from pulp and paper bleaching into a clean-burning synthetic fuel. The biofuel generated with Chemrec's process, dimethyl ether (DME), can be used as a replacement of liquefied petroleum gas (LPG) and diesel. This is particularly significant in view of the ecological impacts of biofuels production and the disruption caused to food production, as brought out by recent studies. A study European Union (EU) has shown that second-generation biofuels such as DME made from biomass gasification provides the highest GHG reduction for the lowest cost. In the Chemec's technology, gasification process that turns black liquor into a mix of CO, H_2 anCO_2 called synthesis gas or syngas, for short, is adopted. Pulp mills already take care of gathering loads of biomass, and, as a liquid, the waste liquor is easier to feed into gasifier than are solid chunks of biomass. In practice, however, this waste has proved tough to gasify. Black liquor is particularly difficult to deal with because of the highly caustic inorganic chemicals, such as NaOH, employed to break down the pulp. In Chemrec's reactor design, black liquor and pure O_2 injected in from the top feed at $1,800^0$C fireball at the centre of the reactor. Most of the dissolved wood in the black liquor forms syngas and flows out of the reactor.

- **Paper-Pulp Batteries**

Ordinary paper could one day be used as a lightweight battery to power the devices that are now enabling the printed word to be eclipsed by email, ebooks and online news. Researchers at SU Stanford University in California reported successful turning paper coated with ink made of Ag and C-nanomaterials into a "paper battery" that holds promise for new types of lightweight, high performance energy storage. The same feature that helps ink adhere to paper allows it to hold onto the single-walled C-nanotubes and Ag-nanowire films. Earlier research found that Si-nanowires could be used to make batteries 10x as powerful as Li-ion batteries now used to power devices such as laptops. This type of battery could be useful in powering electric or hybrid vehicles, would make electronics lightweight and long lasting, and might even lead someday to paper electronics, the researcher added. Battery weight and life has been an obstacle to commercial viability of electric-powered cars and trucks.

- **Energy from Winery Waste**

American and Indian researchers have come up with a new technology that generates electricity by using the waste from improper fermentation. In accordance to them the technology could provide a new and cost effective way to clean wastewater from wineries and get some vale out of a "bad bottle of wine". Two groups of bacteria available in winery waste were found. One group of bacteria turns unused sugar and unwanted vinegar from improper fermentation into electricity, while the other uses that electricity to spilt water molecules into oxygen and hydrogen, which escape into the atmosphere. Recently a microbial electrolysis cell at a winery in Nap Valley, California has been installed by Bruce Logan, a researcher at PSU. Sheela Berchmans of CERI in Karakudi, TN, also claimed to have generated power by using the same methodology, the LiveScience website reported. Sugars like glucose, alcohols and effluents containg sugars or alcohols can be used (to produce electricity) stated Berchmans, who recently co-authored a paper in the journal of Environmental Science and Technology. In accordance with the report, the two groups of bacteria identified as Acetobacter aceti and Bluconobacter roseus – can spoil wine. The researchers at CERI, who created microbial fuel cells using single cultures of each as well as both together, produced 859 milliwatts of power. It is being hoped that the technology could eventually be scaled up to produce more electricity or help to save electricity that would normally be used to treat wastewater.

- **Cooked by Sun**

Methane, an important constituent of cooking fuel, can now be manufactured in large quantities. All we need is a nanotube catalyst, carbon dioxide, water and lots of sun. Researchers used titanium dioxide to create nanotubes ~135mm wide and 0.1mm long. Steel tubes were filled with carbon dioxide and water vapour covering the ends of the containers with a film of nanotubes. When sunlight fell onto the nanotubes, water and carbon dioxide combined to form methane. The devices generated ~160 micro litres of methane/hour/gram of the nanotubes. This method can not only be an important generator of fuel but it might also help control emissions by using carbon dioxide from sources like a coal plant. The findings were released in the February (2009) 5 issue of *Nature*.

- **Pt-free Fuel Cells**

Fuel cells are, in principle, the most efficient way to convert hydrogen fuel into electricity. Conventional fuel cells consist of two electrodes coated with a Pt catalyst that splits hydrogen fuel into acidic hydrogen ions from one side to the other, creating an external electrical current. The use of Pt makes conventional fuel cells very expensive, but cheaper metals simply can't withstand the harsh acidic environment of the fuel cell. Now researchers in China have come out with a fuel cell that uses a new membrane material and eliminates the need for an expensive catalyst. The polymer used as membrane in the new fuel cell is comparable in structure to the highly conductive polymer Nafion (a sulphonated tetrafluoroethylene coplymer) that is used in conventional acidic fuel cells, but is less expensive than Nafion. The new fuel cell uses a Ag cathode and an anode coated with Ni nanoparticles decorated with Cr as the catalyst. The fuel cell works by reacting hydrogen and oxygen to create hydroxyl ions and water, catalysed by the Ni anode. The hydroxyl ions are conducted across the polymer membrane, generating an external electrical current. At present the power output of the new fuel cell is modest-about 50milliwatts/cm^2 at 60^0C. But the first demonstration of an alkaline fuel cell that does not require expensive metal catalyst, it is an important proof of principle, researchers state.

- **Vitamin C Finds Use in Unfamiliar Terrain**

In a new application for disease-fighting vitamin C, researchers have used it to assemble fibre bundles of Au, Ag and Pt nanoparticles. Such bundles are used in new-age medicine to produce sensors for disease detection, enhancement of optical imaging and even manufacture of cheaper and pollution-checking catalytic converters. According to the report published in Journal of Colloid and Interface Science Vol. 311 No. 1, two methods are developed to produce fibre bundles of metallic nanoparticles with vitamine C. In the first method, ascorbic acid was allowed to degrade in acidic condition to form colourless fibres. Then, separately, made nanoparticles of Au, Ag and Pt were deposited on those fibres. In the second method, ascorbic acid was used as a reducing agent on salts of Au (hydrogen tetrachloroaurate) to form Au nanoparticles and subsequently grown into fibres. Using sophisticated imaging techniques like transmission and scanning electron microscopy, the assembly of nanoparticles forming composite fibre bundles were studied.

- **Hydrogen from Pee to fuel Cars**

Researchers have combined refueling our car and relieving ourselves by creating a new catalyst that can extract hydrogen from urine. The catalyst couldn't only fuel the hydrogen-powered cars of the future, but could also help clean up municipal wastewater as reported by physorg.com. Geradine Botte of OU uses an electrolyte approach to produce hydrogen from urine – the most abundant waste on the earth – at a fraction of the cost of producing hydrogen from water. Urine's major constituent is NH_2CONH_2 (urea) which incorporates four hydrogen per molecule – importantly less tightly bonded than the hydrogen atoms in water molecules. Electrolysis was used to break the molecule apart, developing an inexpensive nickel based electrode to efficiently oxidise the urea. To break the molecule down, a voltage of 0.37V needs to be applied across the cell, which is much less than the 1.23V needed to spilt water.

"During the electrochemical process the urea gets adsorbed on to the nickel surface, which passes the electrons needed to break up the molecule," Botte added *Chemistry World Journal.* Storing pure hydrogen gas requires high pressure and low temperature. New nanomaterials with high surface areas can adsorb hydrogen, but have yet to be produced on commercial scale. MCD is working on a project to generate electricity from urine. For this, it will install around 1000 waterless urinal kiosks around the city. Process involved: Waste is collected from waterless urinals and transported to portable power plants. Water, hydrogen are produced from the decomposition of bio-degradable components of urine. Water is cleaned by reverse osmosis and can be used for industrial purposes, power is generated from hydrogen. 1 litre of urine makes 1kw of power, enough to light a 50W bulb for 20 hours.

- **Fuel: Hydrogen Storage Made Easy**

Hydrogen can now be conveniently used as fuel without the usual hassle of storage and distribution. A method has been developed to produce hydrogen on the spot for internal combustion engines from an alloy of Al and Ga. The alloy with 28 % Al by weight, has the potential to replace petrol given its high efficiency and lower cost o production, stated lead researcher Jerry Woodall of SECEPU, Indiana. The mechanism is based on a simple chemical reaction. When water is poured on the alloy hydrogen gas is released this gas is directly fed into the engine as fuel. The technology produces fuel instantly eliminating the need for transportation and storage. Hydrogen generating fuel cells from Al have an efficiency of 75 % as compared to 25 % of petrol-fed internal combustion engines. Here's how it works. When water is added, Al, which has an affinity towards oxygen, breaks it down into oxygen and hydrogen forming Al_2O_3. The end products of the reaction are alumina and Ga along with water as a result of combustion of hydrogen in the engine. No toxic fumes are produced. Since hydrogen has a low MW, it has to be pressurized or liquefied to provide sufficient driving range. The mass of the tanks needed for compressed hydrogen in conventional engines reduces the fuel economy. In the alloy-fed motors, the chemical reaction is processed in a container, in which the by-products solid alumina with a liquid Ga core remains with water. By recycling this by-product, fresh alloy is manufactured in the best way. The technology is suitable for small internal combustion engines like portable emergency engines, lawn mowers and chain saws.

- **Don't Recycle, Upcycle Plastic**

A marvel of modernity, plastic has become an indispensible part of our daily lives. But repeated reprocessing disposal of plastic waste is environmentally unfriendly, polluting and a potential health risk. A new method proposes up cycling – taking waste and turning it into something of value – the ubiquitous plastic bag and converting it into useful nanotubes. According to V G Pol, a scientist at ANL, Illinois, USA, this method is called "re-mediation". Gram pieces of high density or low density polyethylene are heated at 700^0C for two hours in the presence of a catalyst, cobalt acetate $[(CH_3COO)_2 Co]$ the mixture is allowed to cool. Multi-walled nanotubes grow on the surface on the surface of catalyst surface. Carbon nanotubes are extremely thin with a diameter 10,000x less than a strand of human hair. These hollow cylinders made of C-atoms are extremely strong, have good thermal conductivity and are used in electronics, optics etc.

These nano tubes were used as anode for Li-ion batteries. 1 Upcycled plastic from a grocery bag (3-6gram) can produce nanotubes (1-3gram) enough for one cellphone battery, which could suffice as an anode for one Li-ion rechargeable battery. It's thought that the same technology sans a catalyst could be used to grow spherical 2-10 µm carbon bodies, which have applications in printers, toners, filtration technology and the pain and tyre technology.

- **Green Plastic Engineered**

It has been successfully bio-engineered polymers, completely bypassing fossil fuel based chemicals. This breakthrough opens the way for the production of 'green' plastics on commercial scale. The team from KAISTU, South Korea and LG Chem., led by Sang Yup Lee, focused on PLA (-a bio-based polymer considered a good alternative to petroleum based plastics as it's both biodegradable and less toxicity to humans), the key to producing plastics through renewable resources. Until now PLA has been generated in a two-step fermentation and polymerization, which is both complex and expensive. Now, through the use of a metabolically engineered strain of E coli, PLA and its co-polymers through fermentation have been produced, making the renewable production of PLA and lactate-containing copolymers cheaper and more commercially viable. By developing a strategy which combines metabolic engineering and enzyme engineering, an efficient bio-based one step production process for unnatural efficient PLA and its copolymers have been developed.

UNCONVENTIONAL WASTEWATER TREATMENT STRATEGIES

- **Zinc Removal with Old News Paper**

Could the old news papers piling up in the storeroom help treat wastewater? Experiment has hown how newspapers can be used to remove heavy metals from industrial waste water. This experiment focused on the connection between newspaper pulp and Zn. Used newspaper was processed in a $NaHCO_3$ (Sodium bicarbonate) solution to remove ink and other chemicals before being washed thoroughly. From there, the treated pulp was mixed with effluent from the electroplating industry that contained Zn, one of the leading sources of environmental pollution. The treated pulp was able to adsorb a significant amount of the Zn, leading researchers to conclude that the method was successfully applied for Zn removal and it was also a potential adsorbent for Fe, Cu, and Mn. While one of the most common elements on earth, Zn is dangerous in large concentrations. It finds use in antirust coatings, batteries and mixed into alloys and compounds that are used to make paint, wood preservatives, and ointments. Electroplating, which coats a metal that is electrically conductive with a thin layer of anther metal, often creates wastewater with high concentrations of dissolved Zn. While research into these treatments is still on, there is hope that it could be applied to industrial scales. Newspaper pulp is not the first waste product to show potential in filtering heavy metals from effluent water. Materials such as bamboo pulp pink bark, peanut shells and saw dust from teak, spruce and mango trees have all been tested at various times for their ability to adsorb heavy metals in waste water, and the results have been promising.

- **Green Solution to Turn Turbid Water Clear**

Tamarind seed kernel powder, discarded as agricultural waste, is an effective agent to make municipal and industrial wastewater clear. The present practice is to use Al-salt to treat such water.

It has been found that alum increases toxic ions in treated water and could cause diseases like Alzheimer's. On the other hand kernel powder is not-toxic and is biodegradable and cost effective. For the study, four flocculants (chemicals that cause colloids and other suspended particles in liquids to aggregate, forming a floc) namely tamarind seed kernel powder, mix of the powder and starch, starch, and alum were employed. Flocculants with slurries were prepared by mixing measured amount of clay and water. The result showed aggregation of the powder and suspended particles were more porous and allowed water to ooze out and become compact more easily and formed larger volume of clear water. Starch flocks on the other hand were found to be light weight and less porous and therefore didn't allow water to pass through it easily. The study establishes the powder's potential as an economic flocculants with performance close more established flocculants such as $K_2SO_4Al_2(SO_4)_3$. $24H_2O$ (potash alum). The findings of the study were published in December (2007) issue of *Bioresource Technology*.

- **Seaweed to Remove Chromium from Leather Effluent**

Two cost effective and eco-friendly techniques to remove Cr from the effluent discharged by tanning units have been developed by the researchers of CLRI, Chennai. The metal exists in its highly carcinogenic hexavalent form Cr (VI) in the effluent. Currently, chemical precipitation methods are employed to remove Cr, but they lead to the formation of chrome-bearing solid wastes, whose disposal again is a problem. Other methods available like membrane separation and ion exchange are expensive and also generate solid waste containing Cr. One of the method uses H_2O_2 (Hydrogen peroxide) with a zeolite (a porous substance) and organic Cu-complex based catalyst to remove Cr (VI). This process removes Cr ~5x as fast as the other methods. Being porous, zeolites offers far more sites for the reaction to occur, enabling recovery of Cr in less than one hour at 60°C. Studies on commercial tannery wastewater, indicates that the catalyst can be recycled without any large change in its efficiency. The second method uses cheap, abundantly available seaweed, *Sargassum wegtii*. The seaweed added to a chrome tanning solution fully removed the heavy metal in 6hours. A maximum uptake of 35 mg of Cr/gm of seaweed was reported. Later, the chrome-loaded seaweed were used to make $Cr_2(SO_4)_6$ (chromium sulphate), which is a major tanning agent as reported in journal *Environmental Science and Technology*38 (1), 2004. These methods are of special significance to the small and medium leather enterprises due to the cost effectiveness and environmental sustainability.

- **Junk Iron to Clean Polluted Water**

In 1983 the entire Mianus river bridge in Connecticut, US, collapsed when the bearings rusted internally. Rusting thus proved to be a bane. But a bane can be turned into a boon. A team of researchers from China used scrap iron to treat industrial wastewater contaminated with excess of N, P and organic dyes. In wastewater stable and unoxidised scrap develops a strong tendency to react with the pollutants and makes them more biodegradable. In other words while the iron oxidizes (rusts) it helps clean up the polluted water. In a series of experiments carryout since 2001, Luming Ma from TU, China and Wei-xian Zhang from LU, UK, successfully used scrap iron to treat wastewater from petrochemical, textile and pharmaceutical industries. During the full-scale application of the process in 2006, the iron-based reactor was connected to the biological treatment plant to be used as a treatment preceding the biological clean-up.

It was found that N removal had gone up from 13 to 85 %. P removal increased from 55.6 to 63.3 % and up to 80.4 % of the colour was reduced. This partial degradation of polluted water using scrap iron helped in turn completely biodegradable. Conventional technologies like bio-treatment and chemical precipitation are either ineffective or expensive. In chemical precipitation, chemicals are added to wastewater. They react with the contaminants and settle down. The wastewater is then decanted. But this process requires continuous addition of chemicals and produces large amounts of sludge which is expensive to be disposed off. Bio-treatment proves ineffective due to the highly toxic nature of the pollutants. The scrap iron technology is cheaper since iron scraps are readily available. It would be environmentally beneficial in providing iron scraps with a better role than simply dumping them in the junkyard.

- **Copper Removal with Peanuts**

For cleaning wastewater, peanut shella are an effective tool. The agricultural waste removes poisonous Cu ions from industrial wastewater. Though the industry uses many chemical methods to remove heavy metals from wastewater, most of them are highly expensive. This method seems to be cheaper and eco-friendly. Peanut shell cleans 95 % of Cu ions. Waste water from electroplating, pulp and paperboard industries contain Cu and affect marine and human life. For example, it can damage human liver. The study by Duygu Ozsoy and colleagues in the department of environmental engineering at the MU in Turkey was published in the *International Journal of Environment and Pollution,* 31 (1 and 2), 2008. Some other plants and plant products too have been used to clean wastewater. *Erythrodontium barteri*. a moss, removes 97 % of Cu from wastewater, says astudu done at OOU in Nigeria, published in the International *Journal of Physical Sciences,* 2 (11), 2008. The biomass waste traps all the positively charged heavy metal ions, the study explains.

- **Recovery of Cr from Tannery Effluent**

In leather industry, tanning is the main process that protects leather against some environmental effects such as microbial degradation, heat, sweat or moisture. ~ 90% tanneries in the world use Chromium salts as tannage materials because of the excellent properties of the Cr-compounds in the tanning. During the tanning process, Cr forms crosslinks between the collagen fibres and the resulting hides have a good mechanical resistance, and extraordinary dying suitability and a better hydrothermic resistance in comparison with hides treated with vegetable substance. However, only 60% of the total Cr reacts with the hides. The rest of the Cr remains in the tanning effluent and are subsequently sent to a tannery wastewater management plant where the Cr salts end up in the sludge. Cr and other pollutants in the sludge can be released to the water bodies and thus the disposal of tannery sludge has becoming one of the major environmental problems of the tannery industry. One long term solution appears to be recovery and recycling of Cr from it. As traditional chemical recovery methods are associated with high cost and toxic products, there are needs for clean, nontoxic and environment friendly technologies. TERI in collaboration with DU has developed a unique Cr recovery process following green chemistry approach. A range of Cr accumulator plants and microbes are shown in Cr rich tannery effluent, using least amount of different resources, harvested and finally digested them in least amount of mineral acid with minimal use of energy to bring the accumulated Cr into solution.

The Cr rich acid solution is then passed through a specially designed reactor containing reusable metal specific resin compounds to adsorb maximum amount of Cr from the acid solution. Cr impregnated resin is then washed with specific quantity of mineral acid to recover Cr in pure form. Recovery of Cr > 99% has been achieved through this green chemistry approach.

INTEGRATING GREEN CHEMISTRY INTO INDUSTRIAL PRACTICE

There have been rapid changes within the industry in all spheres of activity: research, technology, manufacturing, trade and services, and community interface. Innovations in technology are focusing shifts in raw material, energy usage and material balance as well. Researches in laboratories are complementing modern tools on the shop floor in the market place. Rational design of chemicals has become an intensive are of research. New approaches to technology development center on maximization of techniques. Green chemistry principles have steadily found acceptance in several processes and products.

Replacement of reagents has led to positive improvements in several processes. Phosgene replacement in chemical synthesis has been a major focus area for the industry after the Bhopal incident. Since the 90s major strides have been made in the replacement of phosgene to make isocyanates. Du Point commercialized a process for the manufacture of isocyanates by direct carbonylation of amines with CO. CO_2 has also been commercially used to make isocyanate. MCC developed a dehydrating agent (O-sulphobenzoic acid anhydride) for the highly selective conversion of amines and CO_2 into their corresponding amines. This also enables elimination of phosgene. The manufacture of polycarbonates by molten state of Bisphenol A and diphenylcarbonate as reported by ACC is another striking example of elimination of phosgene. ECC developed a process that uses direct carbonylation of methanol using CO, eliminating use of Phosgene.

a. Alternative reaction conditions: Catalysis to the fore

Catalysis has become the key to designing new synthetic pathways avoiding routes which conventionally yielded low specificity and high wastes. Transition metal, metal oxide, and chiral metal complexes are used as potential alternative catalysts. Application of photochemical catalysis in the production of Friedel-Crafts acylation is another example. This reaction avoids traditional use of corrosive and sensitive acid chlorides.

- **Zeolite Catalysis: fascilitaing cleaner processes**
- **Bio-catalysis: revolutionizing synthetic processes**
- **Pd catalyzed reaction**
- **Non conventional catalyst systems**
- **Chemo & Biocatalytic conversions**

b. Alternative chemical design

c. Alternative reaction processes

- **Super critical fluids**
- **Solid sate processes**

Biocatalysis: Through metabolic engineering an *Escherichia coli* K12 microorganism produces 1,3-propanediol in a simple sugar fermentation process developed by DuPoint and Genencor.

Bipol, the co-polymer – poly-3-hydroxybutyrate-3-hydroxyvalerate, a natural-based polyester developed by ICI is produced from wheat carbohydrate by fermentation using *Alcaligenes eutrophius.* Modified enzymes expected to improve both yields and product properties are developed by Metabolics. Mitsubishi Rayon uses enzyme 'nitrile hydratase' for acrylamide.

A. Leveraging green engineering

a. Energy efficiency

b. Designing inherently safer processes

c. Waste reduction/ reuse

d. Process intensification

Process intensification (PI) is about adapting the process to the chemical reaction, choosing the technology best suited to each step of the process and adapting the size of equipment to the reaction.

e. Process integration: A new approach to waste minimization

f. Process simulation

B. Waste reduction algorithm

Waste reduction (WAR) algorithm developed by EPARREL, Ohio is a significant accounting method for [pollution generation that introduces a yardstick for comparing pollution generation of different processes, which was not possible by other methods. The (WAR) algorithm also provides a systematic design model to determine the pollution index of a product, defined as the amount of waste produced per unit mass of product. PARIS is a new logarithm for replacing hazardous solvents that has found wide application.

C. SYNGEN program

The possibility of designing alternative pathways to produce the same product needs to be explored while designing the process. This requires identification of environmentally benign pathways. EAR is a mathematical tool to systematically synthesize environmentally acceptable reaction sequences. The SYNGEN program, is a synthesis design program which generates the shortest synthetic pathway for a given target molecule from a catalogue of commercially available organic feedstock. There are other similar programs commercially supplied for regulatory and educational purposes, and to sensitize practitioners to the potential environmental impacts of alternative synthetic pathways of target molecule.

A PERSPECTIVE ON TWO DECADES OF INDUSTRIAL GREEN CHEMISTRY AND TECHNOLOGY INNOVATIONS

There has been marked progress in the design and development of greener chemistries and technologies since 1980s. Across the spectrum of chemical industry and allied segments, companies have invested in green chemistry research and commercial expansion. The key principles of green chemistry have found application in diverse sectors such as life sciences, crop protection chemicals, fine chemicals, paints and coatings, adhesives, polymers, etc. applications of green chemistry methods such as biotechnology, polymer technology, renewable, solvent free processes, catalysts, safer processes and alternative synthesis have all been leveraged by companies in their quest for developing sustainable chemistry models.

Many of these have been recognized by USA's President's Green Chemistry Awards and documented in detail by USEPA. To give insight into methodologies and approaches adopted by corporate sectors, some of outstanding examples of innovative green chemistry in these application categories are briefly profiled below.

A. Biotechnology

(a) Eastman Chemical Company: Synthetic pathway

Esters are an important class of cosmetic ingredients comprising emollients emulsifiers and specially performance constituents, and are manufactured using strong acid catalysts at high temperatures. However, this process produces undesirable byproducts demanding energy-intensive purifications. In 2005, Eastman synthesized a variety of esters via enzymatic estrifications at mild temperatures. The estrifications are driven to high conversion by removing the coproduct, usually water from estrification of an acid or a lower alcohol from transestrification of an ester. The high specificity of the enzymatic conversions and low reaction temperatures minimize the formation of byproducts, increase yield, and save energy. Eastman's biocatalytic process is an improvement in terms of quality, yield, cost and environmental footprint compared to conventional chemical syntheses. Leading cosmetic companies are currently evaluating many of Eastman's new esters, including emollient esters made from rice bran oil and glyceride emulsifiers.

(b) Dow AgroSciences LLC (Limited Liability Company) : Greener products

Spinosad, a combination of spinosyns A & D, is effective against insect pests on vegetables. However, there have been few green chemistry alternatives for insect-pest control in tree fruits and tree nuts. Dow AgroSciences developed spinetoram. A significant advancement over spinosad that extends the success of spinosad to new steps. The discovery of spinetoram involved the novel application of artificial neural network (ANN) to the molecular design of insecticides. Spinetoram has a lower environmental impact than do many current insecticides because both its use rate and its toxicity to non-target species are low.

(c) Codexix, Incorporated: Reaction condition

Atorvastatin calcium is the active ingredient of Lipitor®, a drug that lowers cholesterol blocking its synthesis in the liver. The key chiral building block in the synthesis of atorvatatin is ethyl (R)-4-cyano-3-hydroxybutyrate, known as hydroxynitrile (HN). Traditional commercial processes for HN require a resolution step with 50% maximum yield or synthesis from chiral pool precursors. They also require hydrogen bromide (HBr) to generate a bromohydrin for cyanation. All previous commercial HN processes form extensive byproducts, needing high-vacuum fractional distillation to purify the final product. Codexis designed a green HN process around the exquisite selectivity of enzymes and their ability to catalyze reactions under mild and neutral conditions to yield high-quality products. Codexis developed three specific enzymes using state-of-the-art, recombinant-based, directed evolution technologies to provide the activity, selectivity, and stability required for a practical and economic process involving fewer unit operations than earlier processes, most notably obviating the fractional distillation of the product. It provides environmental and human health benefits by increasing yield, reducing the formation of byproducts, reducing the generation of waste, avoiding hydrogen gas, reducing the need for solvents, reducing the use of purification equipment, and increasing worker safety.

The Codexes process is operated by Lonza to manufacture HN for Pfizer's production of atorvastatin calcium.

(d) Archer Daniels Midland Company/ Novozymes: Synthetic pathways

ADMC and Novazymes are commercializing enzymatic interestrification, a technology that has a tremendous positive impact on public health by reducing *trans* fatty acids besides eliminating the waste streams generated by the chemical interestrification process which is the most effective way to decrease the *trans* fat content in foods without sacrificing the functionality of partially hydrogenated vegetable oils. Enzymatic interestrification processes have many benefits over chemical methods, but the high cost of the enzymatic process and poor enzyme stability had prevented its adoption in the bulk.

(e) Bristol-Myers Squibb Company: Synthetic pathway

The complexity of the Paclitaxel molecule makes commercial production by chemical synthesis from simple compounds impractical. BMSC developed a semisynthetic route to paclitaxel from the naturally occurring compound 10-deacetylbaccatin III (10DAB) which contains most of the structural complexity (8-chiral centers) of the paclitaxel molecule. The semisynthetic process is complex requiring 11 chemical transformations and 7 isolations. The process also presents environmental concerns, requiring 13 solvents along with 13 organic reagents and other materials. BMSC developed a more sustainable process using the latest plant cell fermentation technology (PCFT). Compared to the semisynthesis from 10-DAB, the PCFT has no chemical transformations, thereby eliminating 6 intermediates.

(f) University academics: Synthetic pathways

Nontoxic glucose is employed as a starting material, which, in turn, is derived from renewable carbohydrate feedstock, such as starch, hemicelluloses and cellulose. Besides, water is the primary reaction solvent, and the generation of toxic intermediates and environment-damaging byproduct is avoided. Most commercial synthesis of adipic acid use benzene derived from the benzene-tolune-xylene (BTX) fraction of petroleum refining, as the stating material. In addition, the last step in the current manufacture of adipic acid employs a nitric acid oxidation resulting in the formation of nitrous oxide as a byproduct. The Draths-Frost synthesis of adipic acid, developed by Karen M Draths & John W Frost of Michigan State University, begins with the conversion of glucose into cis, cis-muconic acid using a single, genetically engineered microbe expressing a biosynthetic pathway that doesn't exist in nature. Yet another example of the Draths-Frost strategy for synthesizing industrial chemicals using biocatalysis and renewable feedstock is their synthesis of catechol which is an important chemical building block used to synthesize flavors (e.g., vanillin, eugenol, isoleugenol), pharmaceuticals (e.g., L-DOPA, adrenaline, papaverine), agrochemicals (e.g., carbofuran, propoxur), polymerization inhibitors and antioxidants (e.g., 4-t-butylcatechol, veratrol). The Draths-Frost synthesis of catechol uses a single, genetically engineered microbe to catalyze the conversion of glucose into catechol, which accumulates extracellularly.

B. Polymer technology

(a) Cargill, Incorporated: Chemical design

Cargill has successfully developed biobased polyols for several polyurethane applications, including flexible foams, which are the most technically challenging.

Cargill makes BiOH™ polyopls by converting the carbon-carbon = bonds unsaturated vegetable oils to epoxide derivatives and then further converting these derivatives to polyopls using mild temperatures and ambient pressure. BiOH™ polyopls provide excellent reactivity and high levels of incorporation leading to high-performing polyurethane foams.

(b) BASF (Baden Aniline and Soda Factory) Corporation: Green reaction

BASF has invented a new urethane acrylate oligomer primer system. The resin cross-links with monomer (added to reduce viscosity) into a film when he acrylate =bonds are broken by radical propagation. The oligomers and monomers react into the film's crossed-linked structure, improving adhesion, water resistance, solvent resistance, hardness, flexibility and cure speed. The one-component nature of the product reduces hazardous waste and cleaning of equipment, which typically requires solvents. The BASF acrylate-based technology requires less complex, less costly personal protective equipment (PPE) than the traditional isocyanate-based coatings.

(c) The Dow Chemical Company (DCC): Green reaction

In recent years the chlorofluorocarbons (CFCs) blowing agents used to prepare polystyrene foam sheet have been associated with environmental concerns such as ozone depletion, global warming, and ground-level smog. The DCC has developed a novel process for the use of 100% CO_2. Polystyrene foam sheet is a useful packaging material offering high stiffness-to-weight ratio, good thermal insulation value, moisture resistance, and recyclability.

(d) DuPoint: Green reaction

DuPoint is a integrating biology in the manufacture of its newest polymer platform, DuPoint Sorona® polymer. Combining metabolic engineering with polymer science, researchers are introducing a microbial process in a business that has historically relied solely on traditional chemistry and photochemical feedstock. This achievement, comprising biocatalytic production of 1,3-proppanediol from renewable resources, offers economic as well as environmental advantages. The key to the novel biological process is an engineered microorganism that incorporates several enzyme reactions, obtained from naturally occurring bacteria and yeast, into an industrial host cell line. For the first time, a highly engineered microorganism will be used to convert a renewable resource into a chemical at high volume.

(e) Biofine, Inc, (now Biometics, Inc.): Chemicals from waste

Biofine has developed a high-temperature, dilute-acid hydrolysis process that converts cellulogic biomass to levulinic acid (LA) and derivatives. Cellulose is initially converted to soluble sugars, which are then transformed to LA. Byproducts include furfural, formic acid, and condensed tar, all of which have commercial value as commodities or fuel. Feedstock used includes paper mill sludge, municipal solid waste, unrecyclable waste paper, waste wood and agricultural residues. LA serves as a building block in the synthesis of useful chemical products. Markets already exist for tetrahydrofuran, succinic acid, and diphenolic acid (DPA), all of which are LA derivatives. DPA is synthesized by reacting LA with phenol. DPA has the potential to displace Bisphenol-A, a possible endocrine disruptor, in polymer applications. Brominated DPA shows promise as an environmentally acceptable marine coating, while dibrominated DPA may find use as a fire retardant.

C. Renewable resources

There are several innovative technologies developed that use a renewable resource in place of a petroleum-based one: two of the key technologies and their developers are cited here.

Argonne National Laboratory

Low-cost carbohydrates fermentation technology produces lactic acid and ethanol, the feedstock for ethyl acetate ester, a solvent.

Donlar Corporation (now NanoChem Solutions, Inc.)

A process to replace polyacrylic acid by aspartic acid, an amino acid, as the feedstock for the biodegradable thermal polyaspartic acid, was developed.

D. Safer chemicals

The industry also made key strides in design of safer chemicals, a few of which are listed here.

The Proctor & Gamble Company and Cook Composites & Polymers Company together developed Sefose® oils made from sucrose and fatty acids. The oils are formulated with Chempol® MPS alkyd resins to produce safer alkyd paints.

Jeneil Biosurfactant Company developed biodegradable, low toxicity rhamnolipid biosurfactant (glycolipid) substitute for synthetic or petroleum-derived surfactants.

Albright & Wilson Americas (now Rhodia) developed tetrakishydroxymethyl phosphoneium sulphate (THPS) biocides, a new class of environmentally benign antimicrobial pesticides. These biocides replace chlorinated isothiazolones.

E. Solvents

NovaSterlis Inc. used supercritical CO_2 and peroxide for sterilization of delicate biological materials.

SC Fluids, Inc. used supercritical CO_2 to remove photoresist from semiconductor wafers, replacing hazardous solvents and corrosive chemicals.

Dow Chemical Company used CO_2 to replace CFCs as the blowing agent to make polystyrene foam.

F. Solvent free processes

Eastman Chemical Company used solvent free enzymatic estrifications to make a wide variety of esters for cosmetics and personal care products.

Headwaters Technology Innovation used solvent-free process to make hydrogen peroxide directly from hydrogen and oxygen using a novel palladium-platinum (Pd/Pt) catalyst.

Cargill Dow LLC (now NatureWorks LLC) used solventless lactide synthesis process by continuous distillation, polymerization of polylactic acid (PLA) in the molten state, and recycling of PLA.

G. Alternative solvents

Argonne National Company developed fermentation and a membrane process to make ethyl lactate. The process replaces the traditional organic solvents based processes in many applications.

Merck and Co., Inc. used an asymmetric catalysis of unprotected enamines to produce β-amino acids.

H. Synthetic processes

Merck and Co., Inc. developed a convergent synthesis of aprepitant, the active ingredient in Emend®, with half the synthetic steps, almost double the yield, and a reduction of ~80% in both raw materials and waste.

Siid-Chemie Inc. developed a synthesis of solid oxide catalysts with virtually no wastewater discharge, no nitrate discharge, and little or no NO_x emissions.

Pfizer, Inc. redesigned the synthesis of sertraline, the active ingredient of Zoloft®, with only one synthetic step, a single benign solvent, an improved catalyst and selective crystallization.

Lilly Research Laboratories developed the synthesis of LY3000164, a drug candidate for the treatment of epilepsy, using a yeast-mediated asymmetric reaction, eliminating nonrecycled metal, and significantly reducing solvent use.

Flexsys America LP used nucleophillic aromatic substitution for hydrogen (NASH) reactions eliminating chlorine from synthesis of a commodity chemical, 4-aminodiphenylamine, reducing organic waste by 74% inorganic waste by over 99%, and wastewater by over 97%.

BHC Company (now BASF Corporation) redesigned the synthesis of ibuprofen with half the synthetic steps, ~80% atom utilization, and almost no waste.

Monsanto Company redesigned the synthesis of disodium iminodiacetate, the keyintermediate in Round-up™, using a catalytic dehydrogenation route with fewer process steps, increased yield, no formaldehyde or hydrogen cyanide, and essentially no waste.

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NEED OF GREEN CHEMISTRY IN EDUCATION AND RESESRCH

Green chemistry is a responsible way using science and engineering that strive to improve the public image of chemistry, not as a goal in itself but as a consequence of its achievements.

As an example, a survey conducted by ITRC, Lucknow, India; revealed that >70% of colors used in eatables were azodyes which are non-permitted by PFARs. WHO expert's CFA (Committee on Food Additives) has replaced these non-permitted colors in CII, meaning that the data for long term effects are unavailable/ inadequate for these days. Likewise, there are number of chemicals used in daily life as preservatives, soft drink preparations, and culinary recipes etc. which are unsafe for human health.

PERSPECTIVE AND FATE OF GREEN CHEMISTRY

For the promotion of green chemistry, it's imperative to create a brand of green thinkers. Green chemistry should be of upfront consideration. Scholars of all levels must be made aware of the introductory ethics and philosophy of green chemistry. Educators should possess procedures and methodologies and need to equip themselves with training material, tools and similar infrastructures besides collaborations. For a successful implementation more and more green-school programmes as is run by CSE, New Delhi, must be created. Support in terms of tax incentives and awards for promoting green ideas. Information, technologies transfer and approaching beyond sustainability would be welcome step in promoting the green chemistry. Green Chemistry has the potential of wiping out the possible occurrence of tragedies like Bhopal Gas by paving way for safe eco-friendly environment.

There is utmost need to emphasize on creating awareness about green chemistry not only amongst the chemists and scientific community but also industries and commercial institutions. Leading countries like USA, UK, Japan, Italy, Australia and other developed nations have given green chemistry top priority with a view to safeguarding their environment and economic interests. In India, it's in the inception stage and has assumed rapid strides embracing catalysis, benign solvents, renewable feedstock, green nanomaterials, biodegradable polymers and others. Educating the next generation of researchers and training in green techniques occupies a central theme in the outreach activities [Xu et al., 2012, Xu et al., 2012, Yamada et al., 2012].
There is no doubt that the emerging area of green chemistry has identified scientific principles, approaches, and methodologies that have demonstrated the most positive aspects of chemistry in industry. While the success of green chemistry thus far seem quite large in terms of quantitative benefit to human and environment, they are merely the tip of the iceberg when compared to the potential. To reach this full potential, greater awareness, adoption, and development of green chemistry practices are necessary Industries are also started discovering that when their professional chemists are knowledgeable about pollution prevention concepts, they are able to identify and implement effective pollution prevention technologies. For this reason, Green Chemistry should be a part of the regular studies in schools, colleges and research institutes and if it's allowed to grow throughout the curriculum, scholars will rise to the challenge and work to invent a safer upcoming. But if we aren't cautious, if we drive scholars away from these pursuits, then we will have no one to solve these problems, and that could be worst unintended consequence of all

THE WAY FORWARD: INDIA ON LEARNING WHORL

Industrial green chemistry and technology initiatives have made significant progress since the late 1980s. However, radical improvements are needed in process design, including new reactor configurations and integration of operation both within and between enterprises. Industry needs more than a mere demonstration of a new technology. It needs strategies to implement the technology backed by the knowledge to evaluate the business case. Downstream segments such as pharmaceuticals, consumer chemicals and specialty chemicals, with high environmental foot print, have a long way to go in leveraging green chemistry principles. There are several questions pertaining to sustainable development practices, which still need to be answered. These relate to assessment of green performance measurement and diagnostics to evaluate alternate synthesis, and sustaining the performance. Regulations and legislations are powerful drivers for green chemical technology. They drive innovations in chemical research and manufacturing. They open up avenues for innovative solutions and create opportunities for profitably deploying green chemical technology. Those companies which can foresee regulatory trends and develop appropriate business strategies will survive. In India, initial forays into green chemistry and engineering began as everywhere else in the late 1980s. Indian companies looked for ways to reduce waste generation, in sectors such as dyestuffs, textile and leather processing, fine chemicals, etc. these initiatives were followed by recovery by chemicals from waste stream, and rationalization of energy and water use.

It was only during the post economic liberalization phase, with India emerging as an export hub that ISO 18000 and GMP certifications, to name a few, ushered a new approach in the way the chemical industry functioned. Demand for products with low environmental footprint by overseas customers led to improvements in products and processes. India chemical companies also saw the promise of green chemistry practices. The Industry associations such as ICC took the first few steps to orient and train its members through awareness programs.

Though the 90s and beyond, the Indian chemical industry explored all options to rationalize their manufacturing operations and bring about incremental innovations in synthesis, product design, reaction engineering, mass transfer and heat transfer operations. Local Indian companies in the area of crop protection and pharmaceuticals reported small innovations in green chemistry practices. Fine chemical companies made some progress in alternative reaction conditions and media and improvised on the original processes. In the early years of this decade there were concerted efforts in green chemistry practices in universities and institutes of chemical research. Laboratories under the CSIR have all made significant progress in green chemistry: NCL, Pune (catalysis, renewable platforms, new drug design, micro reactor technology, nanotechnologies, etc); IICT, Hyderabad, (drug design, greener reaction and catalysis, etc.); CLRI, Chennai (replacement of hazardous processes); and CMRI, Bhavnagar (renewable sources). Institutes such as the IITs around the country (reactor design, heat and mass transfer, etc.) and ICT, Mumbai (catalysis, separation technologies and biotransformation, etc.) have made significant contributions towards green chemistry and technology practices. In recent years, The Government of India has taken several steps to encourage green chemistry and technology development, one of which was to set a TFGC. Education in green chemistry in India is still an area of concern: there is a need for the development of learning and teaching material in the Indian context. It's imperative to introduce principles as part of learning chemistry at the secondary school levels and colleges. Today, chemical sciences and engineering curricula lack appropriate green chemistry and technology orientation. Indian industry, academia and the government need to collaborate to take green chemistry and technology to the next level of growth

CONCLUSION

Green chemistry focuses on the reduction, recycling, and/or elimination of the use of toxic and hazardous chemicals in production processes by finding creative, alternative routes for making the desired products that minimize the impact on the environment. Green chemistry is a more eco-friendly green alternative to conventional chemistry practices. The green chemistry movement is part of a larger movement ultimately leading to a green economy- namely sustainable development, sustainable business and sustainable living practices. Green chemistry can contribute to achieving sustainability in three key areas. First, renewable energy technologies will be the central pillar of a sustainable high-technology civilization. Second, the reagents used by the chemical industry. Third, polluting technologies must be replaced by benign alternatives. The aim of the article is to acquaint the academicians, researchers, scientists and engineers with values and positive impact of green Chemistry innovation, application and Technology.

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 agreement has to be arrived at between the policy makers and the chemical practitioners in order to give Green chemistry the power it rightly deserve. And a policy needs to be frame to guide the practitioners so that overall efficiency as well as environmental cleanliness is achieved. It is reiterate that the espouse 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 understanding 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 slogan. 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. Conclusively, green chemistry can be considered a bench level practice that also leads to cost reductions and product orientation besides all its other benefits discussed. In the future it will become a strategic tool for companies to rationalize their operations and create value. The firms pioneering innovations in feedstock process and product redesign built around sustainability protocols will lead way in the time ahead. Those firms which can demonstrate that a non-regulatory green chemistry approach be a viable strategy will bring about the much needed mind shifts. Chemical companies are slowly learning to operate and compete in the backdrop of regulatory requirements of countries where they are located. Ensuring IGC practices right from design through dispatch to disposal stages requires long term commitment on the part of industry. The technical, financial, administrative and commercial bottlenecks need to be resolved. Ahead of 2010, the chemical industry has started facing tighter legislative controls and market pressures to confirm to process and product protocols as mandated under various environmental acts. To be able to sustain its growth while complying with future environmental mandates would require a closer audit of existing practices. The challenge in coming years will be to continue to maximize innovations, which meet increasing demands for sustainable products. The knowledge and experience within the sector, together with the new technological advances, needs to be leveraged responsibly. Twenty eight years have lapsed since Bhopal incident and industry has just made a beginning towards sustainability. It's to be seen if the current momentum will be sustained over the next 28 years even as technological, societal and political complexities amplify.

ABBREVIATIONS

USGSE: United States Groups Sapphire Energy; OO: Origin Oil; BCEPA: BioCentric Energy and Petro Algae: GHGs: Green House Gases; O_2: Oxygen; CO_2: Carbon dioxide; NOx: Nitrogen Oxides; CO: Carbon monoxide SO_2 : Sulphur dioxide; TAGs: Triacylglycerols: NAs: Nucleic Acids; CH_3OH: Methanol; MT: Million Tons; R & D: Research and Development; HTP: High throughput; FG: Flue Gas; CFP: Carbon foot print; HCs: Hydrocarbons; T/P: Temperature and Pressure; BOC: Biodegradable Organic Compound; $(CH_3COO)_2Co$: Cobalt acetate; UT: University of Tokyo; UM: University of Massachusetts; MV: Milli Volt; UC: University of Queensland; FBC: Fosters Brewing Company; CSE: Centre for Science and Environment; MCD: Municipal Corporation of Delhi ; UE: University of Edinburgh; HCCPR: Hadley Center for Climate Prediction and Research; IPMA: Indian Paper Manufactures Association; KAISTU: KAIST University; PLA: Polylactic acid; *E: Escherichia; M: Muscodor; G: Gliocladium;* NOx: Nitrogen Oxides: MSU: Montana State University; HCs: Hydrocarbons; GHE; Green House effect; ANL: Argonne National Laboratory; PSU: Penn State University; CERI: Central Electrochemical Research Institute; SECEPU: School of Electrical and Computer Engineering of Purdue University; CLRI: Central Leather Research Institute; LU: Lehigh University; TU: Tongji University; OOU: Olabisi Onabanjo University; NEERI: National Environment Engineering Research Institute; CEPS: Common Effluent Treatment Plant; PERC: Percholoroehylene; PARIS: Program for assisting replacement of industrial solvents; EAR: Environmentally acceptable reaction; EPARREL: Environmental Protection Agency Risk Reduction Engineering Laboratory; LLC: Limited Liability Company; ANN: Artificial neural network; ADMC: Archer Daniels Midland Company; BMSC: Bristol-Myers Squibb Company; PCFT: Plant cell fermentation technology; ICS: Indian Chemical Council; CSIR: Council of Scientific Industrial Research; NPL: National Chemical Laboratory; IICT: Indian Institute of Chemical Technology; CLRI: Central Leather Research Institute; CMRI: Central Marine Research Institute; IIT: Indian Institutes of Technology; ICT: Institute of Chemical Technology; VOC: Volatile Organic Compound; LPG: Liquid petroleum gas; SU: Stanford University; OU: Ohio University; HAP: Hazardous air pollutant; MWF: Metal Working Fluids; EDTA: Ethylenediaminetetrachloroacetic acid; TERI: The Energy Research Institute; DU: Delhi University; E-factor: Environment-factor; E-coat: Epoxy- coat; CCS: Chromate copper arsenate: AQU: Alkaline copper quaternary; PGCCA: Presidential Green Chemistry Challenge Award; AIR: Advanced Image Resource; LPG: Liquefied Petroleum Gas; EU: European Union; REACH: Registration, Evaluation, Assessment of Chemical; OSC: Ohio Soybean Council; ICC: Indian Chemical Company; TFGC: Task Force on Green Chemistry; MCC: Monsanto Chemical Company; ACC: Asahi Chemical Corpoartion; ECC: Enichem Chemical Company; USEPA: United States Environmental Protection Agency; PTC: Phase Transfer Catalysis; MIGS: Microwave Induced Green Synthesis; PTCGS: Phase Transfer Catalysis Green Synthesis; UAGS: Ultrasound Assisted Green Synthesis; BOS: Biocatalysts in Organic Synthesis; APR: aqueous Phase reactions; SSOS: solid State organic Synthesis; VILGSs: Versatile Ionic Liquids as Green Solvents; PAFRs: Prevention of Food Adulteration Rules; ITRC: Indian Toxicological Research Institute;

ACKNOWLEDGEMENTS

I am thankful to Dr. Deepak Vyas, Dr. Tulika Chakrabarti, Department of Chemistry, and Dr. Archana Gajbhiye, Department of Biotechnology, Sir Padampat Singhania University, Udaipur, (Raj) for their valuable suggestions and encouragement during this work. My sincere thanks to Dr. Hariram Choudhary, Scientist, Krishi Vigyan Kendra, Athiyasan, Nagaur for providing necessary facilities of laboratory and library. I am also grateful to Dr. R.K. Maheshwari, Department of Chemistry, Nagaur (Raj.) for his valuable advice, help and suggestions during this work.

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