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Green Chemistry

- 1. Green or sustainable chemistry can help us achieve sustainability in three key areas that could form the basis to protect our environment without harming growth and development. These areas include the role of chemists in
 - a. improving process of converting solar energy into chemical and electrical energy
 - b. obtaining the reagents or chemicals used in the chemical industry from renewable resources, instead of obtaining them from oil and petroleum a fast depleting natural resource
 - c. replacing polluting technologies with suitable non polluting ones.

12 Principles of Green Chemistry

Paul Anastas and John Warner introduced the twelve principles of green chemistry in 1998.

These are asset of guidelines for putting green chemistry into practice. With the aim of understanding green chemistry in various processes from research lab, house hold, general life to bulk production these principles will be discussed in detail with suitable examples from each wherever applicable and the reader may be able to get a vivid image of the source of the problem and the green solution to it, so that in future even readers of this article may be able to contribute their share in sustainability.

- 1. Pollution Prevention: By minimizing the waste produced or by using methods that can avoid waste generation pollution prevention can be attained. This could be different for different people.
- 2. Atom Economy: In the process of making one chemical from another, a part of the starting chemical is lost, which comes out as waste. In atom economy, methods have to be designed such that the entire chemical converts into the other without losing any part of it. It should be just like cooking, put all the ingredients in and the food is cooked, without any waste being produced. Few examples from organic chemistry include the famous Grignard reaction and Diels-Alder reaction with atom economy (AE) of 44.2% and 100% (AE is defined as measure of molecular weight of product over molecular weight of reactant). It is a theoretical value used to calculate how atom efficient a chemical reaction will be.

- 3. Less Hazardous Chemical Synthesis: Synthetic methodologies must be designed such that the chemicals used and by-products, if generated, are not or less harmful to human health and the environment. A better example is the formation of alkenes through more safe Grubbs catalyst in comparison with the Witting reaction. It is worth noting that the Grubb reaction though safe is a finding at recent years whereas the Witting reaction is an age-old method that has helped in a large number of synthesis reactions. This example can serve as a better understanding of how a very important method of the past can be suitably substituted with a less hazardous modern method. In this case, the reaction based on Grubb catalyst produces very less waste compared to the Witting reaction.
- 4. Designing Safer Chemicals: Chemical substances (molecules) may process a variety of properties that define their commercial value like their polymerizing tendency, ability to form coatings etc.In the same way, they also exhibit biological activities that may group them into beneficial drug-like compounds or if they are biologically harmful, they may be classified as toxic.In a true sense, all the molecules of our interest that are used as drugs, plastics, paints etc almost always have some toxicity. It is desired that chemists focus on designing safer chemicals, with some previous understanding. Much work has been done in recording structures of molecules and their toxicity data, which could be used to develop molecules with low toxicity.
- 5. Safer Solvents and Auxiliaries: Solvents are substances (generally liquids) that can dissolve a variety of solids and later can be evaporated easily. Solvents have a variety of applications, like dissolving solids for chemical reactions, dissolving paints which after applying on doors evaporate leaving a coat of paint, decaffeinating coffee, separating organic compounds from mixtures etc. It is hard and impractical to think of not using solvents at all which are largely a produce of petrol and oil industry, a non-renewable resource. Solvents also account for the huge quantity of waste generated in synthesis and processes. After evaporating they also contribute to air pollution, along with water and soil pollution. Recovery and reuse is a good option, but demand distillation, which in itself is a power consuming process. Hence, the only option left is to find substitutes for solvents. A few options found and applied in the past include reactions in water, reactions in solid phase, supercritical fluids as solvents and ionic liquids (solvent-like inorganic substances with low evaporation) as solvents. This field is the most actively pursued and may contribute largely to the green aspect of chemistry.
- 6. Design for Energy Efficiency: Rising consumption and heavy future demand on energy that is primarily generated from petroleum and depleting resources has raised serious concerns in the international community. The solution would not lie in digging in more deeper to use up all the available resource, instead it lies in designing energy efficient processes and generating alternative sources of energy production. In line with this, chemists can design reactions that could take place at moderate temperature using catalysts or other methods, thereby reducing more demand on energy. Common man can also contribute to this by using public transportation and more fuel economy vehicles, thereby reducing demand on petroleum and also by allowing fewer amounts

- of pollutants to enter the atmosphere. On the other hand, there is a lot of ongoing research in developing alternate methods of producing energy from non-depleting resources, like solar energy, bio fuels, wind power, geothermal energy, Hydrogen cells and Proton exchange membrane cells. The best studied among these are the solar cells for converting sun light into electrical energy using organic molecules.
- 7. Use of Renewable Feedstocks: This is another field of interest in research and in serious practice these days. Efforts are being out in to produce organic chemicals and related products to be obtained from natural resources other than petroleum and depleting resources. This is not a very novel field to mankind, because since long ethanol has been produced from a variety of sources like sugarcane, beet root, grape etc. So, other products or chemicals can be produced from natural resources. The best substitute for this is the biomass material available from living organisms, like wood, crops, agricultural residues, food etc. Renewable materials that can be obtained from nature include lignin, suberin, cellulose, polyhydroxyalkanoates, lactic acid, chitin, starch, oil glycerol etc. These can be used ultimately to produce chemicals of our interest, like lignin (which can be further used for production of vanillin, DMSO and humic acid), chitin (used to produce chitosan which is later used in water purification, biomedical applications etc). Interestingly, these renewable stocks are mostly leftover waster of other processes like farming, agriculture etc and hence are the cheapest alternatives.
- 8. Reduce Derivatives: This is more applicable to organic chemists working on synthesis of compounds in multi-step synthesis. It is desired that the routes to synthesize a compound be as short as possible utilizing less number of protection and deprotection of sensitive functional groups. It might be a bit challenging to seek better methods of synthesis but in the long run during the course of performing the same reaction of a large scale, the waste minimized by eliminating protection and deprotection may amount to some tons of material thereby contributing hugely to the success of green chemistry. One such process designed in the industry is in Polaroid films, where researchers sought to release hydroquinones at elevated pH, which being highly basic tends to cleave covalent protecting group in the form of a co-crystal was developed. This approach was successful for their purpose but interestingly minimized a lot of waste thus making the process green.
- 9. Catalysis: This can contribute to green chemistry at least in three ways: By lowering the activation energy of a process, by allowing unfavourable reactions to happen, and through bio-catalysis attaining high levels of selectivity at minimal waste, most of which is fast biodegradable and non-polluting. Catalytic reagents also eliminate the need of stoichiometric amounts of it in the reaction. An example of this includes use of nayori hydrogenation in place of DIBAL-H.In another case, Grubbs catalysis was used successfully in olefin metathesis proving unfavourable reactions also happen at ambient conditions and with less waste. Enzymes and whole cell biotranformaton are now taking the stage in selective (regioselective, enantioselective and chemo selective) reactions, with advantage of replacing highly toxic and polluting metal complexes, giving

- high yields, biodegradable, ambient condition reactions, produced from microorganism or animals, giving no waste and biodegradable when discarded.
- Design for Degradation: Most household and routinely used substances are under the scanner in this category and are being worked out rigorously. They include detergents, plastics (poly ethylene bags), paints etc. Some general alternatives are possible in this case, like use of natural cloth or fibre bags instead of plastic bags, using degradable plastic bags, recycling the non-degradable waste bags and plastics etc. An interesting case of pollution and hazard from detergents happened in 1950s when water coming from taps was also foaming due to the presence of tetrapropylene alkylbenzene sulonate (TPPS) accumulated due to an incomplete degradation. It was addressed by making changes in the structure of the molecule (linear alkylbenzene sulfonate, LAS) with retention of surfactant property but easily biodegradable. It is desired that the chemists be able to understand these aspects before hand while designing and synthesizing such compounds, even though it is not a simple task. Trends have now emerged following decades of data collection, which low allow chemists to predict to properties of such compounds beforehand.
- Real-time Analysis for Pollution Prevention: Real time analysis for a chemist is monitoring the progress of a reaction as it happens to find a better point to stop the reaction in order to avoid formation of by-products. By finding the right time to stop, a lot of energy can also be saved which would have been wasted unnecessarily in continuing the reaction beyond the required point. The importance of this concept can be realized only when one imagines a reaction happening at a scale of tons, where saving even a few minutes of electricity would mean a lot. Similarly, by avoiding the formation of by-product, a lot of solvent can also be saved in the process of purification. The other aspect of real time analysis involves analysis a reaction whose sample needs to be run on HPLC, where method optimization to consume minimum amount of solvent and power need to be designed.
- 12. Inherently Safer Chemistry for Accident Prevention: The Bhopal gas incident is the worst reminder of an industrial tragedy. Accidents do keep happening in industries with damage both to human life and environment apart from the monetary loss. It is necessary that the hazard data (toxicity, physical hazards such as explosive or flammability) and global hazards be addressed in the design of chemicals and processes in order to prevent such accidents.

Achievements and Barriers

1. Since its inception, the concept of green chemistry had much impact on design and implementation of new processes. A few examples of drastic changes brought about include large reduction in lead pollution because of replacement of lead in points and batteries with better friendly alternatives, replacement of chlorine with chlorine dioxide leading to significant reduction in endocrine disrupting chemicals such as polychlorobiphenyls etc.

- 2. Howsoever beneficent green chemistry principles might be to sustainability, the practical implementation in large production plants is a daunting task, as it demands a huge change in industrial setup, machinery and pilot plants. In the presence of laws, suitable incentives and necessary financial support to bring in major changes, the industry may be able to turn their processes green but this could take time.
- 3. Awareness of a problem and initiating action towards controlling it is in itself the big leap required in implementing new policies. Green chemistry is also one such step taken towards sustainability and wellbeing of the human race. Only very recently has the science succeeded in stabilizing itself in many fields, but it still emerges in new fields.
- 4. Under these circumstances there is a need to maintain balance between supporting new developments in chemistry and bringing the previously established chemical process under greener and sustainable purview. But this is a slow process requiring considerable efforts. It is hoped that very soon a trend may get firmly established wherein most of the existing chemical processes could become greener and sustainable. *Courtesy: Science Reporter*