B.Sc. Semester – II

Subject: - GE - 202: Green Chemistry

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2.1. Principles of Green Chemistry

1. Prevention

It is better to prevent waste than to treat or clean up waste after it has been created. The first principle of green chemistry is the principle of prevention.

The prevention of waste generation, which is more favorable for humans and the environment, and ultimately cheaper than treating waste and destroying it after it has emerged.

The justification for the introduction of this principle is confirmed by the fact that around 12 billion tonnes of waste, or about 300 million tonnes of hazardous waste for human health and the environment (so-called hazardous waste) are produced annually in the United States. The chemical industry produces 70 percent of the total amount of hazardous waste and the highest organic toxic waste with methanol and xylenes prevailing. Organic waste, which is harmful to humans and the environment, is primarily produced at certain stages of synthesis, so-called. "Dirty reactions" during which toxic reactants and solvents are used, and due to the harsh reaction conditions, a large number of toxic byproducts are formed. These are the most common basic reactions of organic synthesis (halogenation, oxidation, alkylation, nitration and sulfonation) that are applied in different industrial branches.

Although the chemical industry, as well as other chemical manufacturers, have long ago avoided prevention, the interest of green chemistry and the community is precisely to prevent waste generation. However, the absolute prevention of waste generation in practice is virtually impossible since no input raw material can be fully utilized. On the other hand, one waste disposed of represents the final loss of material goods in the circular flow: production consumption. Therefore, any return of material goods to a circular stream represents a pure economic gain and it is necessary to think first whether it is possible to prevent the generation of waste and if it is not necessary to devise the way in which the amount of waste produced in production can be utilized in the best possible way, so it becomes useful.

This approach to the problem has brought positive results: the paint and varnish industry already produces solvent-free paints and lacquers. The detractors industry has already thrown out all phosphorus-containing detergents. Asbestos is no longer used in practice.

2. Atom Economy

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

The principle of Atom Economy is logically linked to the principle of waste prevention, since it requires all raw materials used in production to maximize utilization or inclusion in the final product to ultimately reduce the amount of waste. This means that the chemical synthesis should be designed in such a way that the final product maximizes the input of raw materials or design such synthetic products that will use the entire material used for synthesis in the final product.

The principle of increasing atomic usability was defined in 1991 by Barry Trost of Stanford University. Trost believes that introducing the concept of usability atoms is essentially the prevention of waste at the molecular level. Barry Trost's concept initiated the redesign of existing synthetic reactions until then established on the principle of "making a product regardless of price". These modifications are useful and because they generally lead to increased yields.

There is a known progress in the synthesis of ibuprofen. The main problem of old synthesis (boots process) is low economic cost, because the utilization of input raw materials is only about 40%. In the 1990s a new "green" method of ibuprofen synthesis was developed, involving only three steps, and almost all transitional materials were converted to the product (up to 99%) or regenerated and returned in the process and almost almost eliminated the generation of waste materials And this process is one of the processes of "green synthesis".

The new process has much higher atomic efficiency and almost no waste (waste materials are recycled in the process) thus contributing to pollution prevention. Atom economy is defined as the ratio of relative molecular masses of the desired product and all reactants expressed in percentages.

% of atomic efficiency = (mol of the desired product/mol of all reactants) x 100

3. Less Hazardous Chemical Syntheses

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

Most chemical synthesis reactions, which usually take place in multiple stages, use toxic reagents. Although the product does not contain these toxic substances, there is a risk of its contamination and redesigning these processes is a task of green chemistry.

The Less Hazardous Chemical Synthesis advocates, wherever possible, the creation of synthetic methods for the use and creation of substances that are little or no toxic to human health and the environment. Replacing harmful chemicals with biological enzymes makes many industrial processes cleaner and cheaper.

4. Designing Safer Chemicals

Chemical products should be designed to effect their desired function while minimizing their toxicity. Minimizing toxicity, while maintaining function and efficiency, can be one of the most challenging aspects of designing safer products and processes, and achieving that goal requires understanding not only chemistry but also the principles of toxicology and environmental science.

Designing Safer Chemicals advocates the design of chemical products in a way that reduces their toxicity and maintains their effectiveness. The goal of producing safe chemicals (non-carcinogenic, mutagenic, and neurotoxic) is the balance between optimal performance and chemical product function, ensuring that toxicity and risk are reduced to the lowest possible level. In other words, the use of toxic chemicals should be avoided and replaced inhospitable wherever possible, but should take account of their efficacy.

This principle is used in the development of new insecticides and pesticides that are specific to target organisms, ie they are toxic only to target organisms and decompose into environmentally harmless substances. Another example is the use of highly toxic organic tin-based organic compounds (Sn), previously coated on the outside to prevent the capture of seaweed and plankton. These organic compounds have been replaced by a product called Sea-Nine which is completely degradable and non-toxic.

5. Safer Solvents and Auxiliaries

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

Chromatographic separations, where large quantities of solvents are used, are problematic due to environmental pollution. Most conventional organic solvents are toxic, flammable and corrosive. Their recycling is linked to energy efficient distillation with considerable losses and therefore the development of environmentally-friendly solvents is necessary.

Safer Solvents and Auxiliaries recommends that the process of synthesis be maximally reduced and, whenever possible, avoid the use of auxiliary chemical substances (eg. solvents, separating agents, etc.) When used they should be harmless. According to the principles of green chemistry, the choice of suitable substitutions for organic solvents is based on: worker safety, process safety, environmental safety and sustainability of the process. The solvent should be chemically and physically stable, low volatility, easy to use and easy to recycle.

6. Design for Energy Efficiency

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

The oil crisis in 1973 has initiated the development of a number of processes in which energy savings are taken into account, with the aim of exploiting every kJ of energy in the production process. Following the above-mentioned Principle of Energy Efficiency, whose other name is Design for Energy Efficiency, as a fundamental requirement, minimizes the use of energy.

7. Use of Renewable Feedstocks

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

The seventh principle of green chemistry advocates Use of Renewable Feedstocks wherever it is technically and economically acceptable. For example, it is more convenient to use renewable raw materials than a variety of plastic materials, and then to waste away the waste materials. Because of this, the making of biodegradable plastic materials is a current trend. Biodegradable packaging has a future in the food industry. Numerous factors, including politics and changes in legislation, as well as global demand for food and energy resources, certainly affect the development of biodegradable packaging. The principle also implies the use of renewable energy technologies that include solar energy, wind power, hydropower, biomass energy and biofuels.

8. Reduce Derivatives

Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

One of the key principles of green chemistry in the synthesis of target molecules is to avoid the use of chemical derivatives (Reduce Derivatives). The principle advocates, wherever possible, the avoidance of physical-chemical processes in which blocking and unblocking of appropriate groups during the synthesis are used, that is, whenever possible, the biological processes in the synthesis should be used to avoid synthesis of the products for which they are not there are enzymes to degrade them. If possible, it is necessary to reduce or avoid unnecessary derivatization (group blocking, protection / elimination protection, temporary physicochemical modification) because such steps require additional reagents and can generate waste.

9. Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

In order to protect the environment, the catalysis principle promotes the use of biodegradable catalysts, which imply less energy use, avoiding the use of organochlorine compounds and reducing the use of water or less waste water.

Like all catalysts, enzymes function in a way that lowers the activation energy of an individual reaction, and thus accelerates, up to several million times. In doing so, the enzyme remains unchanged throughout the duration of the reaction to which it affects, and this allows it to become completely unchanged when the reaction comes to an end. Also, enzymes do not affect the relative energy between the reactants and the products, nor to the related reactions.

However, what enzymes stand out among all other catalysts is their specificity in terms of stereochemistry, chemical selectivity and specificity. Compared with non-biological catalysts, biocatalysts have a great advantage given the rate of reaction, catalytic specificity, lower cost, etc., but lack of heat sensitivity and poor stability.

10. Design for Degradation

Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

The principle of creating degradable chemicals and products or design for degradation demands the creation of chemical products that, upon termination of their activity, must be able to convert into products that are harmless to the environment.

Fulfillment of this requirement is possible by changing the technological parameters in the process management and the change of so-called. Auxiliary substances added at certain stages in the production process. The aim is to prevent the formation of harmful substances and to return to production as much waste as possible, which is achieved by recycling.

11. Real-Time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

Traditional analytical chemistry implies large amounts of sample for analysis, abundant use of solvents and energy. With the development of new methods and precision mobile instruments, it is possible that analyzes work with a small sample size at the sampling site and with much less solvent.

The principle of Real-Time Analysis for Pollution Prevention requires further development of analytical methodology to enable real-time monitoring of the chemical production process with the aim of preventing the formation of dangerous substances, ie it is necessary to constantly monitor the production process at each stage Would prevent the occurrence of errors that could lead to the emergence of dangerous substances, harmful to the environment and human health.

12. Inherently Safer Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

The Twelfth Principle of Green Chemistry is the principle of Inherently Safer Chemistry for Accident Prevention. The basic requirement is to reduce the use of substances in chemical processes that can cause adverse effects (explosion, fire and harmful vapor). An example is today the increasing use of supercritical CO_2 that replaces organic solvents and which, unlike organic solvents, is not toxic or explosive and is environmentally acceptable.

Safety can be defined as a control of known hazards by achieving an acceptable level of risk and is achieved at several levels of the lowest use of Personal Protective Equipment. Then it follows the level of Administrative and work practice controls and implies establishing effective procedures, rotating work tasks, adjusting work schedules so that workers are not over-exposed to the impact of dangerous chemicals, etc. The next higher level of security control is the expert Engineering Controls, which implies the implementation of physical process change to reduce contact with hazardous chemicals, isolate the process, use wet methods to reduce dust formation, ventilation, digestion, etc.

2.2. Future trends in Green Chemistry

♦ Green analytical methods

Development of analytics and environmental monitoring leads to better knowledge of the state of the environment and the processes that take place in it. Due to the lytical cycle) belong to environmentally benign procedures, e.g.:

- ✓ Solid phase extraction (SPE),
- ✓ Accelerated solvent extraction (ASE),
- ✓ Solid phase microextraction (SPME)
- ✓ Liquid-liquid microextraction (MLLE), and other microextraction techniques,
- ✓ Ultrasonic extraction,
- ✓ Supercritical fluid extraction (SFE),
- ✓ Extraction in automated Soxhlet apparatus,
- ✓ Vacuum distillation of volatile organic compounds,
- ✓ Mass spectrometry with membrane interface (MIMS).

The extraction of pesticides from soil samples using accelerated solvent extraction is a good example of an analytical procedure fulfilling the rules of green chemistry. This procedure is characterized by many advantages in comparison to classical extraction techniques used for extraction of analytes from complex matrices. The main advantages considering green chemistry are as follows:

- ♦ Reduction of used solvents (up to 95%),
- ♦ Shortening of analysis time (from 16 hours to 10 minutes),

- Savings of energy (the heating of extraction cell of ASE instrument to 100°C by 10 minutes in comparison to 16 hours heating of a plate in Soxhlet apparatus),
- Decreasing exposure to solvents due to shortening of extraction time and to smaller amounts of applied solvents),
- Similar analytical characteristics (precise and analyte recoveries) for smaller sample (ASE).

This procedure can be treated as an alternative to commonly used extraction in Soxhlet apparatus.

♦ Redox reagents

Uses of Green Chemistry in Oxidation Reactions

The improvements which is made in the impact on the environment due to the pharmaceutical and agricultural chemical industry have lagged behind and stalled the progress which is seen in the manufacturing of bulk commodity chemicals. Fine chemicals are prepared by reactions involving many steps which utilize stoichiometric reagents and chiral auxiliaries. The atom economy of manufacturing these is poor. Many of the biologically active compounds which are from the pharmaceutical and agricultural industries are highly oxygenated and are manufactured from the some type of the oxidation reaction. So there is more demand for the more selective oxidation catalysts.

Role of Green Chemistry in Reduction Reactions

Reduction processes reduce the impact of chemicals on human health and on the environment by utilizing environment friendly processes and the reactions processes. The selection of the solvents and chemicals which are utilized for dissolve many of substances within the solution are of very much importance in green chemistry. They form a major source of waste in the industrial chemical manufacturing but careful selection can be used to increase reaction rates and lowering of reaction temperatures.

♦ Green Catalysts

Most of the catalysts are made of toxic substances. These toxic substances such as heavy metals are required in large quantities to convert petrochemicals. These toxic substances can be very hazardous towards human health and environment and can cause a lot of damage. This will be changed by the use of benign substances. Directed evolution-this will help in the creation and development of new and better proteins (enzymes for biocatalysts) in the laboratory. This will replace old synthetic and harmful technologies and cleaner technology will be available for future use which will help in protection of environment.

♦ Green nano-synthesis

The application of the twelve principles of green chemistry in nanoparticle synthesis is a relatively new emerging issue concerning the sustainability. This field has received great attention in recent years due to its capability to design alternative, safer, energy efficient, and less toxic routes towards synthesis. These routes have been associated with the rational utilization of various substances in the nanoparticle preparations and synthetic methods, which have been broadly discussed in this tutorial review. This article is not meant to provide an exhaustive overview of green synthesis of nanoparticles, but to present several pivotal aspects of synthesis with environmental concerns, involving the selection and evaluation of nontoxic capping and reducing agents, the choice of innocuous solvents and the development of energy-efficient synthetic methods.

♦ Green polymer chemistry

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green polymer chemistry is an extension of green chemistry to polymer science and engineering. Developments in this area have been stimulated by health and environmental concerns, interest in sustainability, desire to decrease the dependence on petroleum, and opportunities to design and produce "green" products and processes. Major advances include new uses of bio-based feedstock, green reactions, green processing methodologies, and green polymeric products.

Green polymer chemistry include herein, typically (1) using renewable resources as starting materials for polymer production, and (2) employing green method for the polymer synthesis. As renewable starting materials, the following materials were employed; lactic acid, itaconic anhydride, renewable plant oils, and cardanol. Polymer production using these materials contributes to mitigate the carbon dioxide emission because of their “carbon neutral” nature. As green method, lipase enzyme was mainly used for polymerization catalyst, since lipase is a natural benign catalyst, showing a specific catalysis as well as recyclable character. Polymer synthesis from these materials and the catalyst provided various value-added functional polymers, demonstrating good examples of green polymer chemistry.

♦ Exploring nature

Green Chemistry and Green Engineering are gaining substantial importance in the chemical and pharmaceutical industries and for new technological developments in a great variety of industries. This is the result of their sustainable nature, energy efficiency, reliance on renewable raw materials, less toxic chemicals and consumer products and lower cost.

New green products and consumer items have establish many practical applications in everyday life in recognition of the previous states of environmental pollution by solid municipal waste. All these green-technology ventures are increasingly gaining importance in the face of global environmental degradation in many parts of the Earth and the increasing population.

Scientists and technologists recognize that the rapid industrialization of the past decades has led to widespread global warming, air pollution, depleting natural resources, greenhouse gas emissions, soil erosion, water pollution, and negative impact on sensitive ecosystems. The legislation of a great number of political and environmental initiatives in developed countries in the last decades, encouraged the development of environmentally friendly programmes and green technologies in every aspect of industry. On top of these programmes Green Chemistry and Green Engineering initiated innovative ideas to overturn serious environmental problems, to provide safer products. The most important sectors of the chemical industry, pharmaceuticals, polymers, food and consumer products increased their participation and invested in green technologies. Already there are many examples of successful ventures and products.

♦ Biomimetic

Biomimicry is the science and art of emulating Nature's best biological ideas to solve human problems. The natural world is made up of very good green chemists. Consider animals and how they make their own shelter and get all the food they need from other things in nature. This is all done without having to use any gas or electricity or taking more than they need, and they produce little waste or waste that can be used by other living things.

Many scientists looking for green solutions are turning to nature for answers to some of our problems with chemical processes. For example, the spider's web is coated with one of nature's strongest adhesives, so scientists have recently done studies of what we call "Spider Web Glue." They found that it is made from proteins with sugars attached to the molecules (glycoproteins). The DNA and enzymes in the spider synthesize this glue, and scientists are working now to find ways to mimic this process. Biomimicry and green chemistry complement each other incredibly well.

♦ Proliferation of solvent-less reactions

Environmental concerns in research and industry are increasing the pressure to reduce the amount of pollutants produced, including organic solvents whose recovery is mandated by evermore strict laws. Hence, the challenge for a sustainable environment calls for clean procedures, which can avoid the use of harmful solvents. "Neat reaction technique" is an alternative environmentally benign solvent-free approach that eliminates the use of solvent from the reaction. These no-solvent reactions prove to be advantageous for environmental reasons and also offer benefits of shorter reaction times when coupled with MWI or ultrasound due to their uniform heating effect.

♦ Non-covalent derivatization

Future Trends in Green Chemistry includes oxidation reagent and catalysis comprised of toxic substances such as heavy metals showing substantial negative effect on human health and environment which can be changed by the use of benign substances, Non covalent derivatization, Supramolecular chemistry research is currently on going to develop reactions which can proceed in the solid state without the use of solvents, Biometric multifunctional reagents, Combinatorial green chemistry is the chemistry of being able to make large numbers of chemical compounds rapidly on a small scale using reaction matrices, Proliferation of solvent less reactions helps in development of product isolation, separation and purification that will be solvent-less as well in order to maximize the benefits.

♦ Biomass conversion

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

(i) The carbohydrate economy provides a rich source of feedstock for synthesizing commodity.

(ii) A continuous process and apparatus converts waste biomass into industrial chemicals, fuels and animal feed. Another process converts waste biomass such as municipal solid waste, sewage sludge, plastic, tires and agricultural residues to useful products, including hydrogen, ethanol and acetic acid.

(iii) A fermentation method for the production of carboxylic acids.

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

(v) A method for mass producing taxol by semi continuous culture of Taxus genus plant.

- **emission control**

Organic light emitting diodes (OLEDS) an example of new lighting technologies produce more light with lower energy consumption.