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Implementation of Green Chemistry in Chemistry - A Review

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Abstract: This paper presents implementation of green chemistry in various aspects of chemistry to overcome the problems of health, safety for workers in addition to the environmental problems are associated with compounds from their manufacturing, use and disposition as waste. Green chemistry is the new and rapid emerging branch of chemistry. Green Chemistry is the practice of chemistry in a manner that maximizes its benefits while eliminating or at least greatly reducing its adverse impacts by the application of 12 principles. Twelve principles of green chemistry focused on methods that deals with prevention of waste, maximize atom economy, less hazardous chemical synthesis, metathesis, designing safer chemicals, using safer solvents and auxiliaries, use of renewable Feedstocks, use of softer catalysts other than heavy metal catalysts, use of biocatalysts, avoid the production of chemical derivatives, develop energy efficient synthesis, development of safer chemistry methods for accident prevention. Green chemistry is also interested for research and alternative innovations on many practical aspects of organic synthesis in the university and research laboratories of institutes.

Keywords: Green Chemical reactions, Green Chemistry in polymer manufacture.

I. INTRODUCTION

Chemistry is the science of matter. Without the persistent efforts of chemists and the enormous productivity of the chemical industry, nothing approaching the high standard of living enjoyed in modern industrialized societies would be possible. It cannot be denied that in years past, and even at present, chemistry has been misused in many respects, such as the release of pollutants and toxic substances and the production of non biodegradable materials, resulting in harm to the environment and living things, including humans.

The practice of chemistry in a manner that maximizes its benefits while eliminating or at least greatly reducing its adverse impacts has come to be known as green chemistry. Green Chemistry is the new branch of chemistry which involves pulling together tools, techniques and technologies. It is helpful to chemists and chemical engineers in research, development and production for development of more eco-friendly and efficient products which may also have significant financial benefits.

Green Chemistry with its 12 principles would like to increases the efficiency of synthetic methods, to use less toxic solvents, reduce the stages of the synthetic routes and minimize waste as far as practically possible. Green Chemistry is also interested for research and alternative innovations on many practical aspects of organic synthesis in the university and research laboratories of institutes.

By changing the methodologies of organic synthesis health and safety will be advanced in the small scale laboratory level but also will be extended to the industrial large scale production processes through the new techniques. Another beneficiary of course will be the environment through the use of less toxic reagents, minimization of waste and more biodegradable by-products.

II. IMPLEMENTATION OF GREEN CHEMISTRY IN CHEMISTRY

1. IONIC LIQUIDS AS GREEN SOLVENTS:

The ions in these ionic liquids are composed of large organic molecules composed of skeletons of numerous carbon atoms bonded to other atoms and having a net charge. The charges on the ions in such compounds is much less concentrated than in simple inorganic compounds like NaCl, the large ions move readily relative to each other in the ionic crystal, and the compound is liquid at low temperatures. A common example of an ionic liquid compound is decylmethylimidazolium hexafluorophosphate, which is a liquid at temperatures above 40˚C, the temperature of a very hot summer’s day. The ionic liquids are rather easy to recycle, adding to their green character. In addition to their applications as solvents for chemical synthesis media, ionic liquids may be useful for isolating pollutants.

2. HYDROGEN PEROXIDE AS GREEN REAGENT:

Despite the evil nature of concentrated solutions of hydrogen peroxide, it can be regarded as a green compound in more dilute solutions, such as the 3% hydrogen peroxide commonly used to kill bacteria in treating wounds. Among its green applications, dilute hydrogen peroxide makes an effective and safe bleaching agent that is much safer to handle than elemental chlorine commonly used for bleaching and that does not produce the potentially toxic byproducts that chlorine generates. And even though it kills bacteria, hydrogen peroxide can be pumped underground to serve as an oxidant for acclimated bacteria that attack wastes that have been placed in or seeped into underground locations.

3. ACETIC ACID AS GREEN ALTERNATIVE:

Acetic acid made by the fermentation of carbohydrates is an excellent green alternative to stronger acids, such as sulfuric acid. Yeasts can convert the carbohydrates to ethanol and other microorganisms in the presence of air convert the ethanol to acetic acid by the same process that vinegar, a dilute solution of acetic acid, is made from cider or wine. The production of acetic acid is a green process that uses biological reactions acting upon renewable biomass raw materials. As a weak acid, acetic acid is relatively safe to use, and contact with humans is not usually very dangerous. Another advantage of acetic acid is that it is biodegradable, so any of it released to the environment does not persist.

4. ALTERNATE REACTION PATHWAYS IN GREEN CHEMISTRY:

Green chemistry involves making decisions about alternative chemical reactions to choose a reaction or reaction sequence that provides maximum safety, produces minimum byproduct, and utilizes readily available materials. Large quantities of materials and energy are expended in converting petroleum hydrocarbons to partially oxidized compounds used as raw materials. For example, ethanol can be made from ethane taken from petroleum and natural gas by a series of chemical reactions for which the net process is the following:

$$2C_2H_6 + O_2 \rightarrow 2C_2H_6O$$

This transformation requires relatively severe conditions and a net loss of energy.

A greener alternative is to use glucose sugar produced by photosynthesis to grow yeasts that produce an ethanol product.

$$C_6H_{12}O_6 \rightarrow 2C_2H_6O + 2CO_2$$

It is the process that occurs under room temperature conditions. In addition to making ethanol, this fermentation process yields carbon dioxide in a concentrated form that can be used for carbonated beverages, supercritical carbon dioxide solvent, or pumped underground for tertiary petroleum recovery. The protein-rich yeast biomass produced in fermentation makes a good animal feed additive.

5. YIELD AND ATOM ECONOMY IN GREEN CHEMICAL REACTIONS:

Yield was defined as a percentage of the degree to which a chemical reaction or synthesis goes to completion and atom economy was defined as the fraction of reactants that go into final products. e.g. preparation of HCl gas by reaction between sodium chloride and sulphuric acid

$$2NaCl(s) + H_2SO_4\,(l) \rightarrow 2HCl\,(g) + Na_2SO_4(s)$$

Percent atom economy = Mass of desired product / Total mass of product × 100

Mass of desired product = 2 × (1.0 + 35.5) = 73.0

Total mass product = 2× (1.0 + 35.5) + (2×23.0 + 32.0 + 4×16.0) = 215

Percent atom economy = 73.0/215 × 100 = 34.0%

This result shows that even with 100% yield, the reaction is only 34.0% atom economical and if it were used as a means to prepare HCl large quantities of Na_2SO_4, a material with only limited value would be produced.

In contrast, the direct reaction of hydrogen gas with chlorine gas to give HCl gas can be carried out with 100% atom economy if all of the H_2 reacts with Cl_2. There is no waste byproduct.

$$H_2\,(g) + Cl_2\,(g) \rightarrow 2HCl\,(g)$$

6. SOLVAY PROCESS- A GREEN CHEMICAL SYNTHESIS:

There are two respects in which Solvay process meet the green Chemical synthesis criteria:

1. It uses inexpensive, abundantly available raw materials in the form of NaCl (brine) and limestone ($CaCO_3$). A significant amount of NH_3 is required to initiate the process with relatively small quantities to keep it going.
2. It maximizes recycle of two major reactants, ammonia and carbon dioxide. The calcination of limestone provides ample carbon dioxide to make up for inevitable losses from the process, but some additional ammonia has to be added to compensate for any leakage.
3. Solvay process also somewhat green with respect to environmental impact as the extraction of the two major raw materials, limestone and NaCl, normally can be accomplished with minimal adverse effects on the environment.

7. GREEN CHEMISTRY IN ORGANIC SYNTHESIS:

With the help of green chemistry six step synthesis of Ibuprofen with the production of secondary by-products, waste and 40% yield is converted into the "greener' method of three steps with final yield 77%,employing the use of recyclable and reusable Raney nickel catalyst. Also the green synthesis of adipic acid uses a new generation of catalysts and biocatalysts. In traditional method for the adipic acid with cyclohexanone/cyclohexanol oxidation by Nitric acid the mass efficiency of the reaction is 55.7% whereas in green method the preparation from cyclohexene oxidized by H_2O_2 in the presence of the catalyst $Na_2WO_4.2H_2O$ (1%) with solvent Aliquat 336 [$CH_3(\nu\text{-}C_8H_{17})_3N$] HSO_4(1%)] the mass efficiency of reaction is 67%. Similarly in the traditional synthesis of maleic anhydrite by using starting material benzene (C_6H_6) and a catalyst which was composed of V_2O_5 and MoO_3 the mass efficiency of reaction is 44.4% whereas in the green method using starting material n-butane and catalyst $(VO)_2P_2O_5$ the Mass efficiency of reaction is 57.6% . Microwave and ultrasound-assisted applications in organic synthesis are interesting to realize the potential of the synthetic method with low energy requirements, less waste, no use of solvent. Another organic chemical that potentially can be produced by the action of transgenic microorganisms on glucose is catechol, used as a feedstock to make flavors, pharmaceuticals, carbofuran pesticide, and other chemicals. Another potentially important organic feedstock that has now been synthesized from glucose using transgenic *E. coli* is 3-dehydroshikimic acid. An abundant source of 3-dehydroshikimic acid could lead to its much wider application as an antioxidant. *Pseudomonas putida* bacteria genetically engineered to carry out several steps in the synthesis of *p*-hydroxybenzoic acid starting with toluene. A key to the process is the attachment at the *para* position on toluene of a hydroxyl group by the action of toluene-4-

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monooxygenase (T4MO) enzyme system transferred to *Pseudomonas putida* from *Pseudomonas mendocina*: The next step is carried out by *p*-cresol methylhydroxylase (PCMH) enzyme from a strain of *Pseudomonas putida* that yields *p*-hydroxybenzyl alcohol followed by conversion to *p*-hydroxybenzaldehyde. The last step is carried out by an aromatic aldehyde dehydrogenase enzyme designated PHBZ also obtained from a strain of Pseudomonas putida and consists of the conversion of the aldehyde to the p-hydroxybenzoic acid product.

8. GREEN CHEMISTRY IN POLYMER MANUFACTURE:

There is a significant potential for the production of pollutants and wastes from monomer processing and polymer manufacture. Some of the materials contained in documented hazardous waste sites are byproducts of polymer manufacture. Monomers are generally volatile organic compounds with a tendency to evaporate into the atmosphere, and this characteristic combined with the presence of reactive C=C bonds tends to make monomer emissions active in the formation of photochemical smog. Some of the environmental and toxicological problems with polymers have arisen from the use of additives to improve polymer performance and durability. The most notable of these are plasticizers, normally blended with plastics to improve flexibility, such as to give polyvinylchloride the flexible characteristics of leather. The plasticizers are not chemically bound as part of the polymer and they leak from the polymer over a period of time, which can result in human exposure and environmental contamination. Though not particularly toxic, these compounds are environmentally persistent, resistant to treatment processes, and prone to undergo bioaccumulation. They are found throughout the environment and have been implicated by some toxicologists as possible estrogenic agents that mimic the action of female sex hormone and cause premature sexual development in young female children. Alternative means of making monomers by green processes have consumed significant effort in the practice of green chemistry. Progress has been made in the green synthesis of adipic acid, one of the two monomeric molecules used to make nylon 66. The conventional synthesis of adipic acid as it has been practiced since the 1940s begins with the addition of H_2 to benzene to produce cyclohexane. Air oxidation over metal catalysts attaches an -OH group to the cyclohexane to make the alcohol, cyclohexanol. This compound is then oxidized with 60% nitric acid, a very severe oxidizing agent, to adipic acid in a process that releases air pollutant nitrous oxide. As a green alternative to the severe chemical conditions required by this synthesis, laboratory studies have shown that genetically engineered *Escherichia coli* bacteria can convert glucose sugar to *cis,cis*-muconic acid, which requires only mild treatment with hydrogen gas to give adipic acid. Developments in genetic engineering have raised the possibility of producing poly(hydroxyalkanoate) polymers in plants. The plant *Arabidopsis thaliana* has accepted genes from bacterial *Alcaligenes eutrophus* that have resulted in plant leaves containing as much as 14% poly(hydroxybutyric acid) on a dry weight basis. Transgenic *Arabidopsis thaliana* and *Brassica napus* (canola) have shown production of the copolymer of 3-hydroxybutyrate and 3-hydroxyvalerate. If yields can be raised to acceptable levels, plant-synthesized poly(hydroxyalkanoate) materials would represent a tremendous advance in biosynthesis of polymers because of the ability of photosynthesis to provide the raw materials used to make the polymers.

III. CONCLUSION

Presently it is easy to find in the literature many interesting examples of the use of green chemistry rules. Green chemistry rules are applied not only in synthesis, processing and using of chemical compounds but many new analytical methodologies are also described with it. The biggest challenge of green chemistry is to use its rules in practice. Great efforts are still undertaken to design an ideal process that start from non-polluting materials. Green Chemistry and Green Engineering provide the tools and alternative materials, processes and systems which will change not only the sustainability of the production of chemical materials, but also their environmental credentials by reducing toxicity and increase recyclability. The intention is to reduce the synthetic stages, to lower the energy use, to increase efficiency with higher yields, to minimize waste, to use renewable starting chemicals.

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