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Green Chemistry in Controlling Environmental Pollution

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ABSTRACT

The use of toxic reactants and reagents affects the environment. The gaseous, particulate substances, solvents and heat added to the environment due to laboratory and industrial chemical processes, reach directly or indirectly by incorporating in precipitation to oceans if these persist in the environment for long time. As a result these cause harm to both territorial and aquatic life. Long lived gases such as CO_2, SO_2, nitrogen oxides gets dissolved in ocean water causing its acidification which has been recently recognized as threat to marine organisms especially marine calcifies. At this stage, the beginning of Green Chemistry was marked. Green Chemistry is defined as environmentally benign chemistry. Green chemistry is one of the most explored topics these days. Main research on green chemistry aims to minimize or eliminate the formation of harmful bi-products and to maximize the desired products in an environment friendly way. The three main developments in green chemistry include the use of super critical carbon dioxide, water as green solvent, aqueous hydrogen peroxide as an oxidizing agent and use of hydrogen in asymmetric synthesis. In order to reduce carbon footprint, the traditional methods of heating are increasingly replaced by microwave heating. It also saves a lot of time. Even food with low carbon footprints is greatly encouraged these days. This paper mainly highlight on applying green chemistry to day to day life in order to control environmental pollution.

1. Introduction

“The Pollution Prevention ACT stated that the first choice for preventing pollution[1] is to design industrial processes that do not lead to the production of waste[2-3]. The environmental protection agency (EPA) defines green chemistry, as the design of chemical products and processes that reduce or completely exterminate the use or generation of hazardous substances. This involves reduced waste products, nontoxic components and improved efficiency. Environmental chemistry is the chemistry of natural environment and of pollutant chemicals in nature, whereas green chemistry particularly tends to reduce and prevent pollution at source [4]. Paul Anastas known as the father of green chemistry has given the term green chemistry in 1991. Main emphasis of green chemistry researchers is to design safer chemicals and chemical processes in order to replace the use and generation of hazardous substances [5].

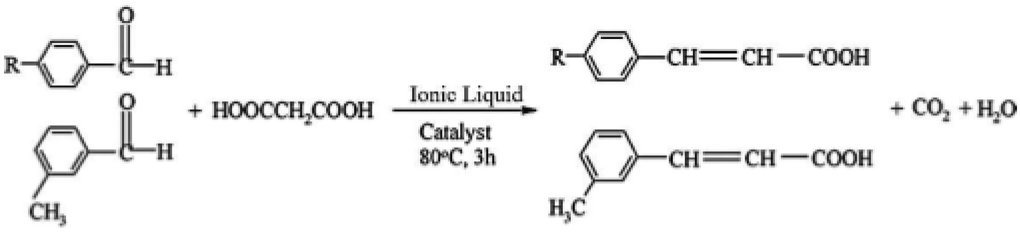
2. Basic Principals of Green Chemistry [6]

1. Prevention: It is better to prevent the production of waste than to treat or clean up waste after it has been generated.
2. Atom Economy: Synthetic methods should be designed to maximize the incorporation of all materials employed in the process into the final product i.e. Reduce waste at the molecular level.
3. Less Hazardous chemical synthesis: Wherever possible, synthetic methods should be designed to use and create substance that possesses little or no toxicity to human health and environment.
4. Designing Safer Chemicals: Chemical products should be designed to perform their desired function while minimizing their toxicity and environmental destiny throughout the design of the process.
5. Solvents and auxiliaries: Safest available solvents must be selected for any given step and organic solvents must be avoided whenever possible.
6. Design for energy efficiency: Choose the least energy demanding chemical method. Ambient temperature and pressure are ideal.
7. Use of renewable feed stocks: Use chemicals which are made from renewable (i.e. Plant based) resources rather than chemicals obtained from depleting resources.
8. Reduce derivatives: Minimize the route of temporary derivation such as blocking group, protecting groups.
9. Catalysis: Use catalytic reagents rather than stoichiometric reagents in reactions.
10. Design for degradation: Design chemicals that degrade and break down into innocuous substances which do not persist in environment at the end of their function.
11. Real time pollution prevention: Monitor chemical reaction in real time, in process and control before the formation of hazardous substance.
12. Safer chemistry for accident protection: Choose and develop chemical techniques and substances that are safer and minimize the potential for chemical accidents, explosions and fires.

Green Chemistry controls environmental pollution by using a variety of green alternatives to conventional methods

Ionic liquids: Ionic liquids are mixtures of anions and cations, molten salts with melting point around 100 degree-Celsius, which can be used as alternative solvents in organic synthesis. They are very promising as alternatives even to organic solvents as their properties can be tuned by proper selection of cation and anion constituents [7-17]. For example

Scheme 1. Simple Aldol reaction using Ionic liquids as solvents[18-20]

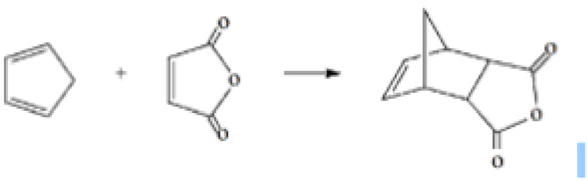


Scheme 2. IL catalysed Doebner condensation

In Doebner condensation, ionic liquids [Bmim]BF4 and [Bpyr]BF4 are used to synthesize αβ-unsaturated carboxylic acid[21-22].

Scheme 3. Michael reaction employing a variety of catalysts[23-28].

Organic Synthesis in Water: Although water is considered a problem for organic synthesis and the purification process and drying in final products is very cumbersome, yet in recent years, water is considered as good solvent for organic reactions. For example- Synthetic routes of the Diels-Alder reactions[29, 35] in which the hydrophobic properties of some reagents make water an ideal solvent. Water as a solvent accelerates some reactions because some reagents are not soluble and provide selectivity.



Scheme-4 Diels-Alder Reaction

Supercritical Carbon-Dioxide and Super-Critical Water: A Super-critical liquid/gas is a liquid/gas at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. The supercritical liquid can effuse through solids like a gas and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density allowing many properties of a super-critical liquid to be fine-tuned. Supercritical liquids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes. Carbon-Dioxide and Water are the most commonly used supercritical fluids. They are known as “Green Solvents” in many industrial processes, providing high yields in many reactions. Supercritical CO2 has been tested in various industrially important reactions, such as alkylations[31], hydroformylations[32], and hydrogenation[33], as an alternative reaction medium. Applications of supercritical CO2 in polymers has been found in polymerization, polymer composite production, polymer blending, particle production, and microcellular foaming. The widest application of supercritical CO2 has been observed in extraction. Solvent free reactions: In most organic reactions liquid solvents are used such as hydrocarbons, chlorinated hydrocarbons, esters, alcohols, ethers, ammonia, carbon disulphide, water etc. based upon its physical and chemical properties, its suitability to the chemical reaction. But the attempt to develop environment friendly, synthetic procedures has projected the need to minimize use of solvents (VOC) which are the major cause of pollution. Some of solvent free reactions such as Tishchenko reaction[34], Reformatsky and Luche reaction[36], Oxidative Coupling reaction of phenols with FeCl3 [37] , Solvent free synthesis of Chalcones [38], etc. are given below.

$$2\ RCHO \xrightarrow{\text{Catalyst}} RCOOCH_2R$$

Scheme 5 : Tischchenko reaction

$$RCHO + BrCH_2COOEt \xrightarrow[\text{NH}_4\text{Cl}]{\text{Zn}} ArCH(OH)CH_2COOEt$$

Scheme 6 : Reformatsky Reaction.

$$RCHO + BrCH_2CH = CH_2 \xrightarrow[\text{NH}_4\text{Cl}]{\text{Zn}} RCH(OH)CH_2CH = CH_2$$

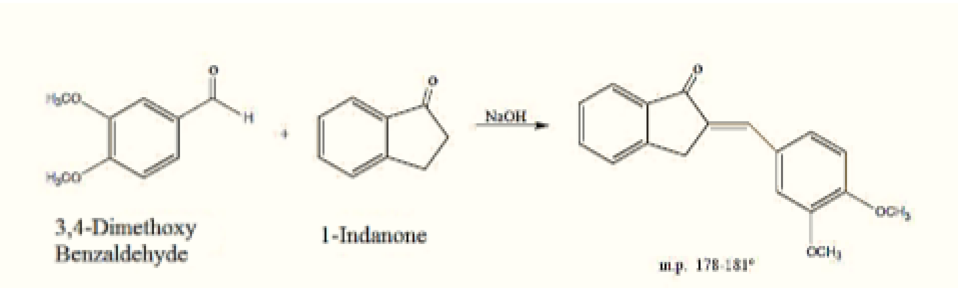
Scheme 7 : Luche Reaction

(2)

Scheme 8 : Oxidative Coupling Reaction of phenols with FeCl

$$C_6H_5CHO + C_6H_5COCH_3 \xrightarrow{\text{NaOH}} C_6H_5\text{–}CH = CH\text{–}CO\text{–}C_6H_5$$

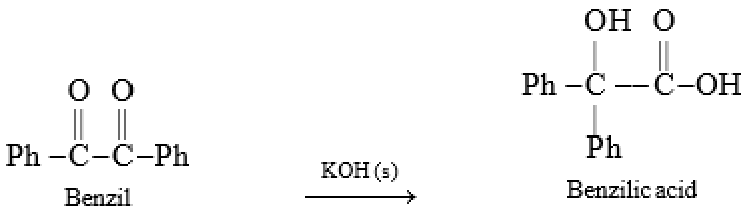
Scheme 9 : Synthesis of Chalcones.



Scheme 10. Solvent free aldol condensation

$$C_6H_5CHO \xrightarrow{\text{Thiamine}} C_6H_5COCH(OH)C_6H_5$$

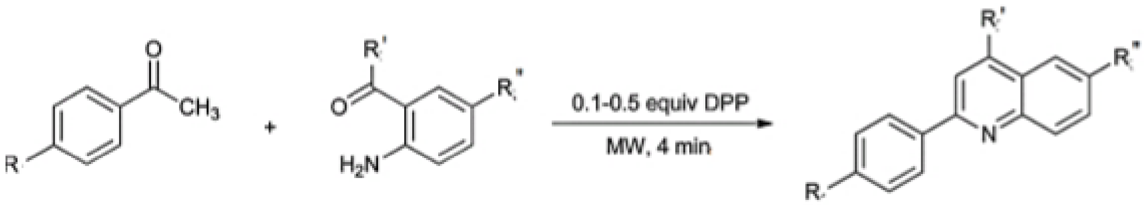
Scheme 11. Solvent free Benzoin condensation



Scheme 12. Solvent free conversion of Benzil to Benzilic acid

The conversion takes place in half an hour on heating the contents on water bath. The same reaction occurs only in one minute by heating in microwave at 540 watt.

Microwave assisted solvent free Organic Synthesis: This technique does not require solvents and are considered "greener" than the conventional methods. Microwave-irradiation in the solid-state is a technique that is being utilized to affect chemical transformations rapidly in contrast to those that have been classically conducted in liquid solutions. The microwaves assisted solvent free reactions can be done in open vessels which prevent the risk of high pressure development within the container and cause explosion. Solvent free reactions also reduce waste discharge. For example microwave-assisted solvent-free preparation of quinoline derivatives by Friedlander coupling condensation between an acetophenone and a 2aminoacetophenone in the presence of diphenylphosphate (0.1–0.5 equiv.) within 4 min. has been described by Kwon [39]. This procedure afforded product yields of up to 85%, whereas the yield obtained with classical heating under similar conditions did not exceed 24%.



Scheme-13. Preparation of quinoline derivatives under microwave in the absence of solvent

$$C_6H_5COCH(OH)C_6H_5 \xrightarrow[\text{MW}]{\text{Zeolite A}} C_6H_5COCOC_6H_5$$

Scheme 14. Oxidation of Benzoin to Benzil without any oxidizing agent

Green Organic Analysis

In conventional organic analysis, organic compound is fused with sodium metal which is very hazardous as may cause fire if come in contact with moisture or water. Sometimes it violently explodes and even strikes the eyes of the students causing damage. A safe and non-hazardous procedure, which can be alternatively performed, has been proposed to use zinc dust and sodium bicarbonate instead of metallic sodium.

Green Qualitative Inorganic Analysis

In classical technique H2S is used, which is highly toxic and has adverse effects on humans and the environment. Increasing awareness concerning a healthy environment, Sidhwani, Tucker ; I Chowdhury have developed a green scheme for detection of cations. NH4+ and K+ are detected in group zero by applying direct tests. Pb2+ and Ag+ are detected by using dilute HCl as their chlorides in group I. Ca2+, Sr2+, Ba2+, and Pb2+ are precipitated as sulphates using Na2SO4(aq) and ethanol in group II. Cu2+, Cd2+, Fe3+, Mn2+, Co2+, Ni2+, and Mg2+ are precipitated in group III as hydroxides using NaOH and H2O2 . The precipitate is treated with NH3(aq) which dissolves Cu2+, Cd2+, Ni2+, Co2+ forming soluble ammines and are grouped as group IIIB leaving behind a residue containing Fe3+, Mn2+, Mg2+ as hydroxides and are grouped as group IIIA. Al3+, Zn2+, Sn2+/Sn4+ as soluble hydroxo complexes and Cr3+ as CrO42- are detected in group IV [51]. Also, the amount of reagents used and thus environmental pollution can be reduced by performing spot tests for cations and anions instead of conventional tests.

Green Quantitative Analysis using flower petal extracts as Indicators

The synthetic indicators like phenolphthalein, methyl orange and phenol red are not only hazardous to health but are also prominent pollutants. The Green Chemistry has proved that these unsafe chemicals can be substituted by the petal extract as an indicator for acid base titration. The accuracy of the observed results has been examined by performing titration between different acids and bases of varying normality using petal extracts which are neither harmful to the environment nor it causes any health hazards e.g. Delonix regia flower petals, Urena lobata, Hibiscus rosa sinensis, Dahlia pinnata etc.[52]

Chemists are also trying to find more environmental friendly and sustainable methods to be used in daily life.Some examples are discussed below.

1. **Biodegradable Plastics**: Non-biodegradable plastics are making a giant heap of waste material on earth. Minnesota makes food containers from polylactic acid called as ingeo. Scientist at nature works converted corn starch into a resin that is just as strong as the rigid petroleum based plastic and is currently used for making containers such as water bottles, yogurt pots etc. BASF developed a compostable polyester film called Eco flux they are using for making fully biodegradable bags made from this film with cassava starch and calcium carbonate. Theses bags completely decompose into water, CO2 and biomass in industrial composting systems. Use of these bags in place of conventional plastics bags, the kitchen and yard waste will quickly vitiate in municipal corporation system[44].
2. **Ecofriendly Paint**: Oil based 'alkyd 'paints give off large amount of volatile organic compounds (VOCs) as it dries and cures. These VOC's have many environmental effects. Procter & Gamble and Cork composites & polymers established a mixture of soya oil and sugar to be used in place of petroleum petrochemicals derived paints resins and solvents which reduced the hazardous volatiles by 50%. Chermpol MPS, paint formulation use these bio based sepose oils to replace petroleum based solvents and create paint which is safer to use. Sherwin William established water based acrylic alkyd paints from recycled soda bottle plastic (PET), acrylics and soya bean oil. These paints give performance benefits of alkyds and low VOC content of acrylics. In alone 2010 enough quantity of these paints were manufactured to eliminate 362,874Kg of VOC's[46-47].
3. **Green Bleaching agents**: Conventionally during manufacturing of good quality white paper, lignin from wood used for it, is removed by placing small pieces of wood into a bath of sodium hydroxide and sodium sulphide followed by its reaction with chlorine. Chlorine during the process also reacts with aromatic rings of the lignin to form chlorinated dioxins and chlorinated furans. These compounds being carcinogens, cause health problems. Terrence Collins of cambegie mellon university developed a green bleaching agent which involves use of H2O2 as a bleaching agent in the presence of some activators such as TAML[42] which catalysis the fast conversion of H2O2 into hydroxyl radicals that cause bleaching. This bleaching agent breaks down lignin in a shorter time and at much lower temperature .It can be used in laundry and results in lesser use of water[43].
4. **Putting out fires the green way:** The conventionally used chemical firefighting foams used worldwide discharge toxic substances into environment contaminating water and deleting ozone layer. A new Foam called pyro cool has now been invented to put out fires effectively without producing toxic substances as in other firefighting materials[49].
5. **Green dry cleaning of clothes:** Percholoroethylene (perc) is the solvent most commonly used in dry cleaning clothes. Perc (Cl2C = CCl2) is suspected to be carcinogenic and it contaminates ground water on its disposal. A new technology known as micell technology is developed by Joseph De Simons[40], Timothy Remark and James Mc clain in which liquid carbon dioxide can be used as a safer solvent along with a surfactant to dry clean clothes. This method is now being used commercially by some dry cleaners. Dry cleaning machines have been modified for using this technology so carcinogen PERC is replaced by green solvent[41].
6. **Turning turbid water clear in green way**: Conventionally, municipality and industrial waste water is made clear by the use of Alum. Alum is found to increase toxic ions in treated water which causes Alzheimer's disease. The tamarind seed kernel powder has been found as effective and economic agent to make waste water clear as alum.
7. **Biofuels:** It can be obtained from biomass which may be obtained from sugar cane, corn, rapeseed, straw, wood, animal and agriculture residues. For example: Bio-diesel which is produced from oil or fat by a process called ‘’ transesterification‘’ when burnt in diesel engine with hydrocarbons is found to reduce the petroleum fuel consumption as well as the generation of toxic gaseous substances[45].
8. **Lighter vehicles preparation, reduced costs and carbon dioxide emission:** The modern synthetic polyesters has been found to reduce the quantity of foam used in the seats of the car, decreasing its weight sufficiently which decreases the fuel consumption and carbon dioxide emission into atmosphere.
9. **New Lighting technologies**: Organic light emitting diodes (OLEDS) an example of new lighting technologies produce more light with lower energy consumption.
10. **Use of Unleaded petrol:** The higher the octane number better is the quality of petrol. Octane number of petrol these days is increased without addition of lead components such as tetra ethyl lead (TEL) .Unleaded petrol is obtained by adding methyl tertiary butyl ether (MTBE) which supplies oxygen of petrol and hence reducing the formation of per-oxy compounds [50].
11. **Use of Nonpetroleum fuels Power Alcohol**: When ethyl alcohol is used in an internal combustion engines, it is called ‘’ power alcohol ‘’. It is mixed with Gasoline in the ratio of 4:1 in order to increase its octane number. As in India ethyl alcohol is prepared from molasses, a dark brown mother liquor residue left after the crystallization of sugar thus an enormous amount of residue is consumed and hence reduces the pollution [48].

12 **Benzol:** It is obtained as side product during coal carbonization. It is also obtained from the fractional

distillation of light oil. It is a mixture of benzene (70%), Toluene (18%) and Xylenes (6%) with some other hydrocarbons. It can be used as a component of motor fuels due to its high anti knocking value and hence it reduces the fuels consumption as well as generation of toxic pollutants.

3. Conclusion

Though many exciting green chemical processes are being developed but there are far greater number of challenges lies ahead. A lot of efforts are being undertaken to design nonpolluting starting materials and to get safer products without side products. Development of better machines and fuels which produce lesser amount of polluting exhaust gases such as CO, CO2, SO2, nitrogen oxides etc. leading to air pollution and ultimately ocean acidification, has been proposed. Use of good fuel and modified green processes will also reduce the addition of heavy toxic metals and other toxic substances to the environment. Solvent free chemical processes or replacement of organic solvents by water reduces the addition of volatile organic compounds (VOC) in the environment. Use of microwave for chemical processes has reduced reaction time as well as amount of heat energy. Reduce, reuse and recycling, the principles of green chemistry will result in decrease of marine debris also in addition topollution in surrounding environment. The greatest challenge is too incorporate the green chemistry in industrial, laboratory and day to day processes in order to control environmental pollution and hence ocean pollution at source. Many successful efforts have been made but still a lot has to be done. This can be achieved by training and educating new generation of chemists. Green chemistry has to be introduced in the syllabus of the students at all levels, so that each individual is made aware to choose greener ways in his or her life.

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