

GREEN CHEMISTRY: AN APPROACH FOR GREENER SYNTHESIS FOR SUSTAINABLE FUTURE

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ABSTRACT

The advancement in chemistry and process design requires environmentally preferable pathways. There is an emergence of extensive knowledge for the systematic and quantitative design tool for green chemistry. An innovative technology can be sustainable in terms of economy and environment. In order to fulfill the environmental mandates, the industries had to install waste handling, treatment, control and disposal systems. Green chemistry provides an opportunity for manufacturers, processors and other users to carry out their work in an environmentally beneficial way. The pollution can be reduced by green chemistry by minimizing hazards of chemical feedstock, reagents, solvents, and products. It ensures that the traditional methods used in chemistry are practiced in a way that brings positive impact on environment without any harm. The innovations in green chemistry and nanotechnology allow both environment friendly and profitable potential to different industries. This paper aims to highlight the components used in green chemistry with different examples and greener approach for the synthesis of sustainable materials for several treatments. Future studies on innovation technologies based on nano-phenomena needs to be done for realistic approach of environment sustainability.

Keywords: Green Chemistry, sustainable chemistry, sustainable materials innovation technologies, environment sustainability.

INTRODUCTION

Green chemistry aims to design and prepare chemical products that are cost competitive and also design to processes which have attained the highest level of pollution-prevention hierarchy by the reduction of pollution. The concept of green chemistry was coined by an American Paul Anastas and attributes to an ideal chemical reaction [2]. The various steps of hierarchy includes **Source reduction and prevention of chemical hazards** by designing products which are less hazardous to human health as well as environment. The **designing of processes** with reduced chemical waste, synthesis using less energy and fewer water supplies, by treatment of chemicals to render them less hazardous before disposal and untreated waste disposal safely in the environment are the various steps followed to sustain green chemistry principles.

12 Principles of Green Chemistry:

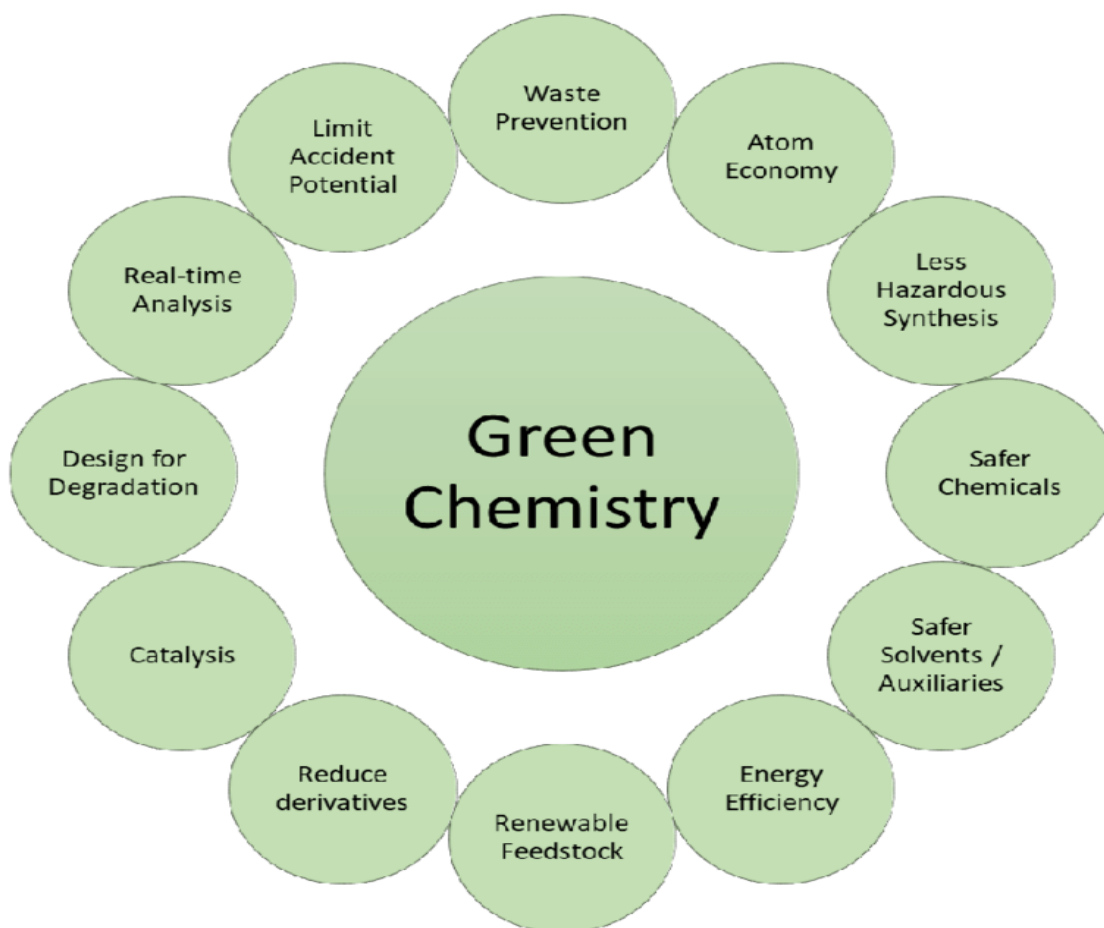


Fig No. 1: Principles of Green Chemistry

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The basic principles involved in Green Chemistry and its applications are

- i. Waste Prevention for proper clean up strategy
- ii. Atom economy maximization for proper design strategies.
- iii. Less hazardous chemical synthesis with low toxicity to humans and environment.
- iv. Design of safer chemicals and products.
- v. Use of safer reaction conditions and solvents
- vi. Increase of energy efficiency in chemical reactions.
- vii. Use of renewable starting materials
- viii. Avoidance of chemical derivatives
- ix. Use of catalyst to minimize waste
- x. Design of chemicals products to degrade after use.
- xi. Real time monitoring and control after synthesis
- xii. Design of chemicals to minimize accidents.

GREEN CHEMISTRY RESEARCH BASIC COMPONENTS

Green Chemistry uses the materials that benefit the environment directly or indirectly. The products are developed which ensures the unforeseen consequences to be minimized [10]. The major research efforts of green chemistry may be broadly classified in different components as

- 1 Alternative starting material
2. Alternative transformations
3. Alternative reaction conditions
4. Alternative final products

1. **Alternative starting Material:** The research efforts in Green Chemistry include alternative starting material as basic component. These materials are environmentally safe with reference to

human health and environment conservation. These are employed to reduce the cost and structural modifications for toxicity reduction and replacement of hazardous materials. The various examples which depict green phenomenon are

a) **Synthesis of Aromatic Amines:** The chlorinated amines which are employed for the synthesis of aromatic amines are known to be persistent bio-accumulates and are environmentally hazardous [8]. The use of chlorinated hydrocarbons can be avoided by employing nucleophilic substitution. The method was given by Stern & coworkers which really solved the concern for the use of chlorinated amines for the commercial preparation of aromatic amines.

b) **Synthesis of Adipic Acid:** According to Frost and Michigan the manufacture of adipic acid, catechol and hydroquinone using glucose in place of benzene

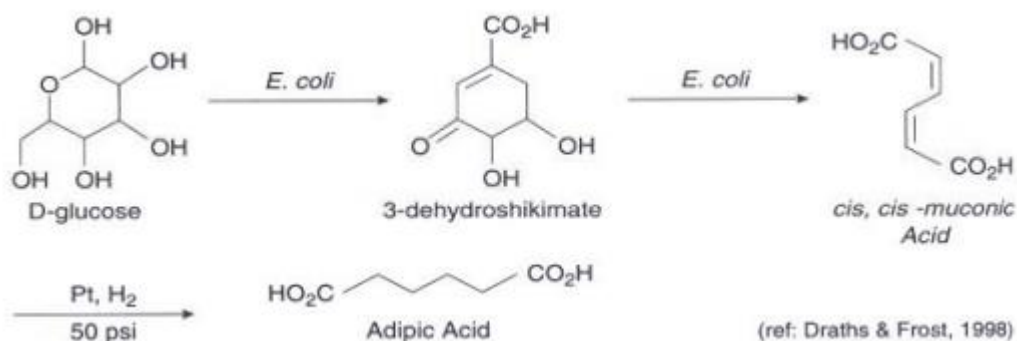


Fig No. 2: Synthesis of Adipic Acid

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c) **Synthesis of iso-cyanates and polycarbonates polymers without using hazardous phosgene:** According to Riley, McGhee and coworkers, elimination of phosgene in the manufacturing of iso-cyanates and polycarbonate polymers by employing a process for the direct combination of carbon-dioxide with amines [12]. Polyurethanes are used in the preparation of cushion mattresses, paints, adhesives and car bumpers. The polyurthranes are generally manufactures from isocyanantes. The reaction of amines with phosgenes is hazardous due to toxicity of phosgene. The experimental conditions for the highly selective synthesis of isocyanates from carbamate anions which are produced by the reaction between amine and carbon dioxide with other dehydrating agents like acetic anhydride, benzoic anhydride.

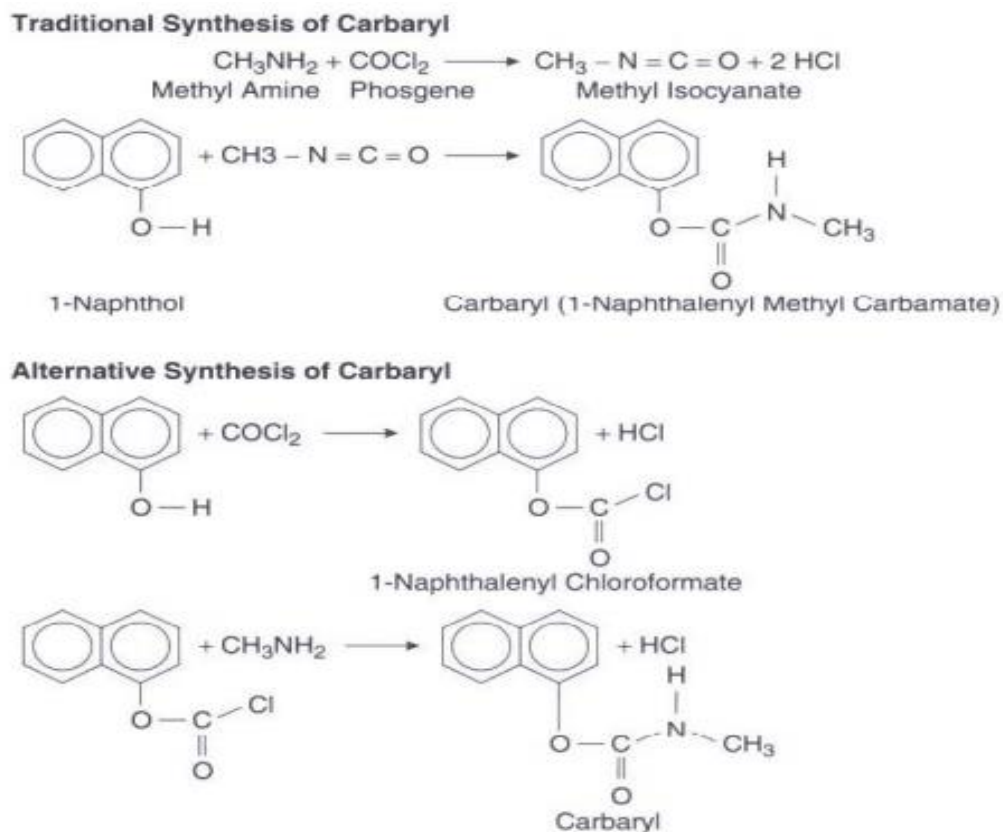


Fig No. 3: Greener Synthesis of Carbaryl

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The ortho-sulphobenzoic acid anhydride is used as a dehydrating agent provided a selective conversion of amines and carbondioxide into isocyanates eliminates the use of phosgenes. This reaction is preceded via nucleophilic attack of carbamate anions at the anhydride subsequently producing isocyanates. According to Koniya et al the synthesis of polycarbonates without using phosgenes was reported [14]. The method utilizes a molten state reaction between bis phenyl dihydroxy compound A and di-phenyl carbonate. The above process is compatible towards green chemistry as it eliminates the utilization of harmful compound phosgene and secondly it is carried out in molten state which eliminates the use of methylene chloride solvent which is also regarded as carcinogenic in nature.

d) **Synthesis of Indigo:** Indigo, a dye can be prepared enzymatically by the removal of side chain of tryptophan to give the compound indole which can be enzymatic dehydroxylated and oxidized

by means of oxygen. Presently indigo is manufactured commercially from aniline which is highly toxic and also produces considerable amount of waste salts which cannot be disposed properly. Yet another greener way can be used to rise as a crop where commercial strain leads to 5 times more indigo production.

2. Alternative Transformations

The toxic reagents can be replaced by benign chemicals to perform certain transformations. The main objective of such efforts is basically done to reduce environmental and human health risks. Some examples of alternative transformations include

- Paquette reported the use of Indium instead of metals where transformation can be carried out in aqueous medium instead of volatile organic solvents [15].
- Many strong methylating agents such as dimethyl sulphate is acutely toxic and carcinogenic in nature. Fundo reported the use of dimethyl carbonate for methylation of acrylonitriles and which is an important reagent in the synthesis of antidepressant drugs. This serves a dual purpose in terms of green chemistry which eliminates the use of toxic dimethyl sulphonate and its high production. Dimethyl carbonate was prepared by the oxidative carbonylation of methanol using carbon mono-oxide and thus avoiding the preparation from traditional method of phosgene and methanol.

3. **Alternative Reaction conditions:** Some of the main alternatives to traditional solvents are

- Supercritical fluid:** the use of SCF $\text{CO}_2/\text{H}_2\text{O}$ and Supercritical CO_2 . These solvents are under investigation for various reactions and promote low cost. The supercritical CO_2 is non toxic and non-inflammable. The solubility of most of the solvents in SCF changes considerably near the critical point. The solute recover is possible by reducing the pressure below the critical point since high molecular weight hydrocarbons are not soluble in SCF.

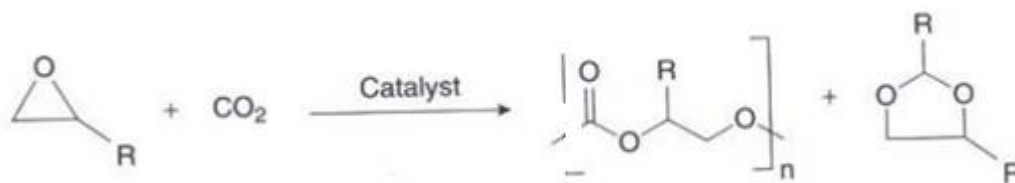


Fig No. 4: Polymerisation using SCF's

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b) **Aqueous solvents system:** Although water is non toxic, non inflammable renewable solvent and the solubility of many hydrocarbons reactants in water has been a limitation. The water in alcohol co-solvent is used in Diel Alder reaction.

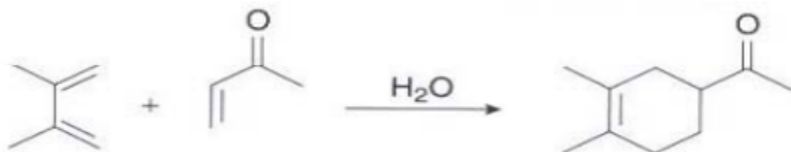


Fig No. 5: Aqueous conditions for Di-Elder reaction

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b) **Immobilised Solvent Materials:** The Hazardous substance under consideration such as tetra hydro furan THF is attached to a polymeric backbone which is chlorinated styrene derivative. This attachment helps in easy recovery and makes it less volatile.

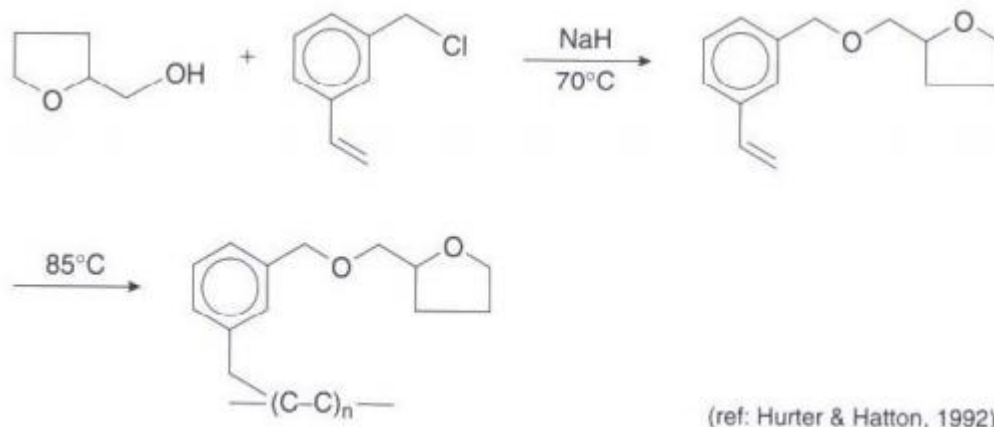


Fig No. 6: Derivatized/Polymeric Solvent Replacement for THF

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4) **Alternative products and target molecules:**

De Vito found that by blocking the alpha position, the ability of nitriles to form an alpha radical is prevented and thereby the toxicity of nitriles is reduced by several orders of magnitude without adversely affecting the ability of nitrile to function as a cross linking agent. The example is the greener synthesis of Ibuprofen shown in Fig. No. 7.

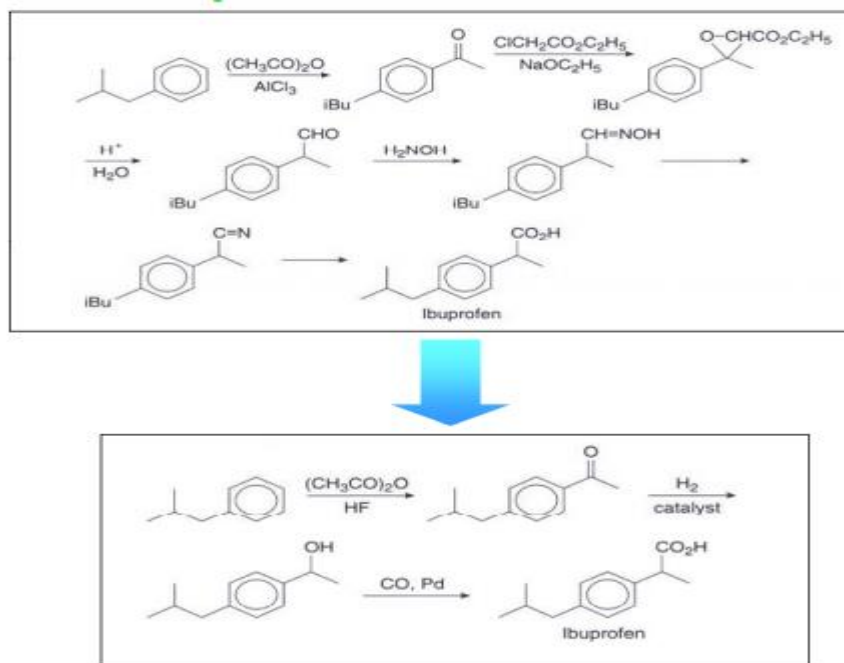


Fig No. 7: Greener synthesis of Ibuprofen

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Functional Group Approaches to Green Chemistry

- Structure activity relationship SAR:** Any chemical used in synthesis may possess some potential risks to human health and environment [17]. It is possible to do the preliminary screening of the environmental impacts of these chemicals. A number of tools can be used to design more environmentally benign chemistries including structural Analysis relationship, identification and avoidance of toxic functional group, reducing bioavailability and design of chemicals for innocuous fate. SAR can be used to detect the structural modifications and this may help to improve the safety. This is definitely a powerful design tool like methyl substituted analog of a substance is highly toxic and the toxicity decreases as we move from ethyl to propyl, therefore it is advisable to increase the

chain length from ethyl to propyl for the design of safer chemical. In cases where the alkyl chain length is not known it is observed that the structure activity relationship is a very powerful design tool.

- b. **Avoidance of toxic functional group:** In case where there is no information regarding the chemical toxicity or the mechanism of toxicity production, and there is assumption that certain reactive functional groups will react similarly where the body or environment is good sometimes. The design of a safer chemical could proceed by removing the toxic functionality but in certain cases it is not possible to do so since it is the functionality which gives the molecule a particular function. In such Cases making the functional group to a non toxic derivative and only releasing the parent functional when required.. For example vinyl sulphone functionality is highly electrophilic and reacts with cellulosic fibres making an affective component of lysine [18]. A variety of toxic effects is associated with this functionality. Sulphones are thus generated only when they are needed by converting a hydroxyl ethyl sulphone into vinyl sulphone.

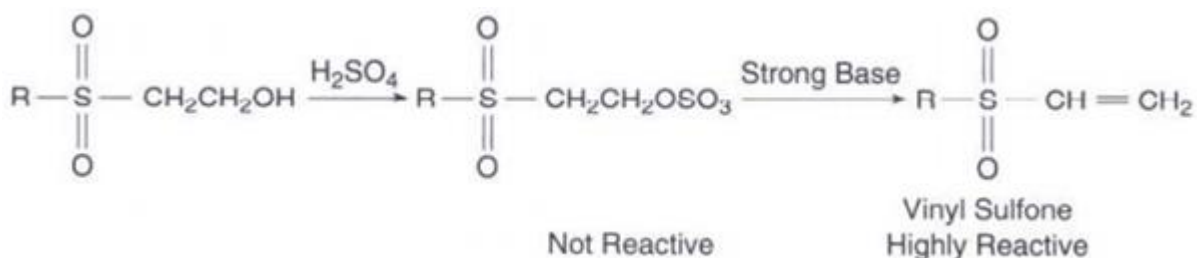


Fig No. 8: Synthesis of Vinyl sulphone

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- c. **Reduce Bioavailability:** The reduction in the bioavailability can be done through the manipulation in the water solubility. This often controls the ability of substances to pass through the biological membranes which may either skin, lungs or gastrointestinal tract.
- d. **Design for Innocuous fate:** It is seen that the chemists usually design substances which were desirable and strong and long lasting. This is disadvantageous as it can result in the accumulation of toxic substances. But the presence of substances for long periods is harmful so they have to be degraded after their useful time period. So it can be concluded that the design of substances should be for a with reference to both hazards and disposal [19].

APPLICATIONS OF GREEN CHEMISTRY

1. Nanotechnological application:

Nanoparticles and the phenomenon of nanotechnology enhance microbial activity so as to remove the pollutants and enhance bioremediation. Nano-remediation reduces the overall cost and clean up time for large scale contaminated sites. Nanoparticles are used as adsorbents and can remove organic and inorganic pollutants. The application of nanomaterials for the conservation of environment is mainly by the use of Nanomaterials for pollution abatement [20].

2. Pharmaceutical Analysis:

The products from natural materials such as palms, coconuts, palm seeds, soy oil are used as starting materials for variety of products like fatty acids, esters, glycerols, long chain alcohol etc. These are used in variety of body care, pharmaceuticals and food products. Palm oil nowadays compete well with mineral oils and even in the production of petrol and natural gas.

3. Environmental remediation and sustainability:

The coupling of biorefinery with existing drying facility for green materials where the biomass is separated into liquid extract and solid residue. This solid residue is processed to produce animal feed, composite, fibre materials and starting materials for some acids [21]. The liquid extract is used for producing proteins and fermentation media. Tonnes of ecoplastics are produced annually from corn waste. These ecoplastics are used for routine packaging like foil or plastic pots and even in T shirts. Starch is degraded to glucose syrup which is eventually converted to lactic acid.

4. Industrial Applications:

The green solvents and supercritical media are fast emerging as promising alternatives for organic solvents of various processes. The initial industrial applications were removal of caffeine for coffee and tea, fat reduction in cocoa, extraction of peanut oil etc [22]. Super critical fluids are also being used in the preparation of well defined polymers, polyamides in paints and varnishes automobile industries. The traditional procedure followed for achieving well defined distribution of grain size is the repeated sieving and sorting. Super critical fluids are also finding applications in nano-electronics in which supercritical carbon-dioxide can replace ultra high purity water [23].

Ionic liquids are also used as green solvents which have the advantage of low vapor pressure. Chloroaluminate compounds are used for electrophilic alkylation, acylation and cationic polymerization. The use of biodiesel is an environmentally friendly and it decomposes without producing any harmful substances and also acts as green propellants.

CONCLUSION:

Green Chemistry is also called sustainable chemistry which is an area of chemistry and chemical engineering focused on design of products, atom economy, less hazardous chemical synthesis, safer chemicals and safer solvents. It has emerged from small grassroots idea into a new approach for scientific based technology. The green chemists are working all over the world for transformation of economy to sustainable enterprise. Approximately 5 billion tones of chemical wastes are released in the environment due to chemical industries every year. The industries also spend huge amount annually for the disposal, treatment and control of these chemical wastes [23]. It also demonstrates the potential to develop modern technologies and latest techniques to minimize the pollution and enable suitable environment measures to promote green chemistry. Thus Green Chemistry is considered to be next Social Movement which can allow creation of Environment commendable civilization.

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