GREEN CHEMISTRY

Introduction

1. Green chemistry is the design of chemical products and process that reduce or eliminate the use and generation of hazardous substances. Green chemistry also called sustainable chemistry.
2. Green chemistry is an area of chemistry and chemical engineering focused on the designing of products and processes that minimize the use and generation of hazardous substances.
3. Whereas environmental chemistry focuses on the effects of polluting chemicals on nature,
4. Green chemistry focuses on technology approaches to preventing pollution and reducing consumption of nonrenewable resources.
5. Green chemistry overlaps with all sub discipline of chemistry but with a particular focus on chemical synthesis, process chemistry and chemical engineering, industrial applications. To a lesser extent, the principles of green chemistry also affects laboratory practice.
6. The overarching goal of green chemistry namely, more resource-efficient and inherently safer design of molecules, materials, products and processes can be pursued in a wide range of contexts
7. The practice of green chemistry must be based upon environmental chemistry. This important branch of chemical science is defined as the study of the sources, reactions, transport, effects, and fates of chemical species in water, soil, air, and living environments and the effects of technology thereon.

History

1. The idea of green chemistry was initially developed as a response to the Pollution Prevention Act of 1990, which declared that U.S. national policy should eliminate pollution by improved design (including cost-effective changes in products, processes, use of raw materials, and recycling) instead of treatment and disposal.
2. Although the U.S. Environmental Protection Agency (EPA) is known as a regulatory agency, it moved away from the “command and control” or “end of pipe” approach in implementing what would eventually be called its “green chemistry” program.
3. By 1991, the EPA Office of Pollution Prevention and Toxics had launched a research grant program encouraging redesign of existing chemical products and processes to reduce impacts on human health and the environment.
4. The EPA, in partnership with the U.S. National Science Foundation (NSF), then proceeded to fund basic research in green chemistry in the early 1990s.
5. The introduction of the annual Presidential Green Chemistry Challenge Awards in 1996 drew attention to both academic and industrial green chemistry success stories.
6. The Awards program and the technologies it highlights are now a cornerstone of the green chemistry educational curriculum.

7. The mid-to-late 1990s saw an increase in the number of international meetings devoted to green chemistry, such as the Gordon Research Conferences on Green Chemistry, and green chemistry networks developed in the United States, the United Kingdom, Spain, and Italy.
8. The 12 Principles of Green Chemistry were published in 1998, providing the new field with a clear set of guidelines for further development. In 1999, the Royal Society of Chemistry launched its journal Green Chemistry.
9. In the last 10 years, national networks have proliferated, special issues devoted to green chemistry have appeared in major journals, and green chemistry concepts have continued to gain traction.
10. A clear sign of this was provided by the citation for the 2005 Nobel Prize for Chemistry awarded to Chauvin, Grubbs, and Schrock, which commended their work as "a great step forward for green chemistry"

Green Chemistry: Future

1. Many challenges still lie ahead, and the solutions will be found not only in the discipline of chemistry but at its interfaces with engineering, physics, and biology.
2. New developments in toxicology such as predictive toxicology and toxicogenomics are making it ever more possible to advance the most important concept in Green Chemistry: design.
3. Green Chemistry must establish a comprehensive set of design principles and interdisciplinary cooperation to move toward routine consideration of hazards as molecular properties just as malleable to chemists as solubility, melting point, or color.
4. The brief history of the field of Green Chemistry is marked with extraordinary creativity and accomplishments in achieving the dual goal of merging superior environmental and economic performance. This has generally been accomplished through the important tactic of improving a single important element or characteristic such as toxicity, persistence, or energy consumption.
5. The powerful reality that is beginning to be realized and that must be exploited in the future is that the Principles of Green Chemistry can be approached as a unified system.
6. Rather than thinking of the principles as isolated parameters to be optimized separately, one can view the principles as a cohesive system with mutually reinforcing components.
7. This approach will be particularly important as we strive to understand the fundamentals of sustainability. While many of the current approaches seek to address important elements of sustainability, e.g., energy, or water, or food, it is important to recognize that all of these elements of sustainability are inextricably linked.
8. Therefore, one important strategy will be to address these interconnected issues at the place where they all intersect: the molecular level. While no one would argue that this makes the challenges easy, it does become conceptually more straightforward through the principles of Green Chemistry.

GREEN CHEMISTRY

Definition

Green Chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical product. .

The term green chemistry is defined as: The invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances.

Looking at the definition of green chemistry,

- The first thing one sees is the concept of invention and design. By requiring that the impacts of chemical products and chemical processes are included as design criteria,
- The definition of green chemistry inextricably links hazard considerations to performance criteria.
- Another aspect of the definition of green chemistry is found in the phrase “use and generation”.

- Rather than focusing only on those undesirable substances that might be inadvertently produced in a process, green chemistry also includes all substances that are part of the process.
- Green chemistry is a tool not only for minimizing the negative impact of those procedures aimed at optimizing efficiency, although clearly both impact minimization and process optimization are legitimate and complementary objectives of the subject.
- Green chemistry, however, also recognizes that there are significant consequences to the use of hazardous substances, ranging from regulatory, handling and transport, and liability issues, to name a few.
- To limit the definition to deal with waste only, would be to address only part of the problem.

In 1998,Paul Anastas(who then directed the green chemistry program at US EPA) and John C. Warner (then of Polaroid corporation) Published a set of Principles to guide the practice of green chemistry. The twelve principles address a range of way to reduce the environmental and heal impact of chemical production and also indicates research priorities for the development of green chemistry

The principles cover such concepts

1. The design of process to maximize the amount of raw material the ends up in product.
2. The use of renewable material feedstock’s and energy sources
3. The use of safe, environmentally benign substances, including solvents whenever possible
4. The design of energy efficient processes
5. Avoiding the production of waste, this is viewed as the ideal form of waste managements.

The Twelve Principles of Green Chemistry

1. **Prevention**

   It is better to prevent waste than to treat or clean up waste after it has been created.

2. **Atom Economy**

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

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.

4. **Designing Safer Chemicals**

   Chemical products should be designed to effect their desired function while minimizing their toxicity.

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.

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.

7. **Use of Renewable Feedstocks**

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

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.

9. **Catalysis**

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

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.

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.

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.

Need of Green chemistry in our day to day lifecycle

- Green chemistry is the new and rapid emerging branch of chemistry.
- The beginning of green chemistry is considered as a response to the need to reduce the damage of the environment by man-made materials and the processes used to produce them.
- Green chemistry could include anything from reducing waste to even disposing of waste in the correct manner.
- All chemical wastes should be disposed of in the best possible manner without causing any damage to the environment and living beings.
- This presents selected examples of implementation of green chemistry principles in everyday life

GREEN CHEMISTRY IN DAY-TO-DAY LIFE

1. Green Dry Cleaning of Clothes

Perchloroethylene (PERC), $Cl_2C{=}CCl_2$ is commonly being used as a solvent for dry cleaning. It is now known that PERC contaminates ground water and is a suspected carcinogen. A technology, known as Micell technology developed by Joseph De Simons, Timothy Romark, and James McClain made use of liquid CO_2 and a surfactant for dry cleaning clothes, thereby replacing PERC.

Dry cleaning machines have now been developed using this technique. Micell Technology has also evolved a metal cleaning system that uses CO_2 and a surfactant thereby eliminating the need of halogenated solvents.

2. Versatile Bleaching Agents

1. It is common knowledge that paper is manufactured from wood (which contains about 70% polysaccharides and about 30% lignin).
2. For good quality paper, the lignin must be completely removed. Initially, lignin is removed by placing small chipped pieces wood into a bath of sodium hydroxide (NaOH) and sodium sulphide (Na_2S).

3. By this process about 80-90% of lignin is decomposed. The remaining lignin was so far removed through reaction with chlorine gas (Cl_2).
4. The use of chlorine removes all the lignin (to give good quality white paper) but causes environmental problems.
5. Chlorine also reacts with aromatic rings of the lignin to produce dioxins, such as 2,3,4-tetrachloropdioxin and chlorinated furans.
6. These compounds are potential carcinogens and cause other health problems.
7. These halogenated products find their way into the food chain and finally into products, pork, beef and fish. In view of this, use of chlorine has been discouraged. Subsequently, chlorine dioxide was used.
8. Other bleaching agents like hydrogen per oxide (H_2O_2), ozone(O_3) or oxygen (O_2) also did not give this the desired results.
9. A versatile agent has been developed by Terrence Collins of Camegie Mellon University.
10. It involves the use of H_2O_2 as a bleaching agent in the presence of some activators known as TAML activators that as catalysts which promote the conversion of H_2O_2 into hydroxyl radicals that are involved in oxidation (bleaching).
11. The catalytic of TAML activators allow H_2O_2 to break down more lignin in a shorter time and at much lower temperature. These bleaching agents find use in laundry and results in lesser use of water.

3. Green Solution to Turn Turbid Water Clear

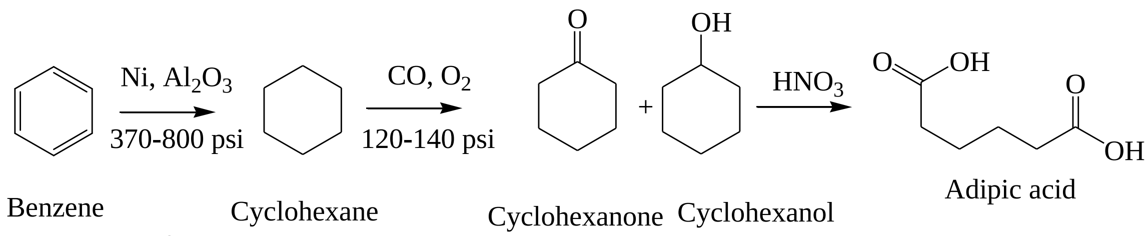
Tamarind seed kernel powder, discarded as agriculture waste, is an effective agent to make municipal and industrial waste water clear.

1. The present practice is to use Al-salt to treat such water.
2. It has been found that alum increases toxic ions in treated water and could cause diseases like Alzheimer's. On the other hand kernel powder is not- toxic and is biodegradable and cost effective. For the study, four flocculants namely tamarind seed kernel powder, mix of the powder and starch, starch ad alum were employed.
3. Flocculants with slurries were prepared by mixing measured amount of clay and water.
4. The result showed aggregation of the powder and suspended particles were more porous and allowed water to ooze out and become compact more easily and formed larger volume of clear water.
5. Starch flocks on the other hand were found to be light weight and less porous and therefore didn't allow water to pass through it easily.
6. The study establishes the powder's potential as an economic flocculants with performance close more established flocculants such as $K_2SO_4Al_2(SO4)_3.4H_2O$ (potash alum)

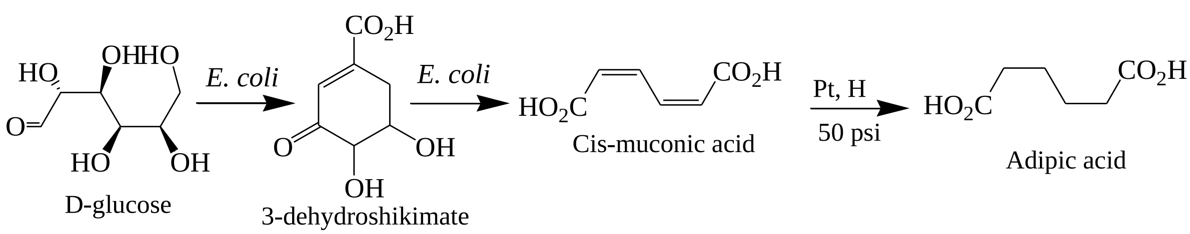
Dr. Vaijinath A. Verma, Dept. of Chemistry, S.S. Margol College of Arts, Science and Commerce, Shahabad, Kalaburagi

Green synthesis

1. Adipic acid (Traditional synthesis)
   i. It is currently produce at around more than10 lakhs liters used benzene for synthesis of adipic acid.
   ii. Adipic acid is a very popular starting material for nylon-6-6 and catechol synthesis widely used in pharmaceutical and pesticide industries



Green synthesis of Adipic acid



This ecofriendly method did not produce toxic waste, moreover, it is yield and reaction mas efficiency is 90 and 67% . Biocatalyst method for the synthesis of adipic acid from D-glucose has also been promoted where generally transgenic bacteria nontoxic stain.

2. Urethane

1. Urethane is required in large quantities for the manufacture of polyurethane a class of number of commercial applications.Urethane is a synthetic crystalline compound used in the manufacture of pesticides, fungicides, cosmetics, and pharmaceuticals.
2. Previously, it was considered to be an effective veterinary anesthetic. “Ethyl carbamate” and “ethyl urethane” are synonyms for urethane.
3. Though polyurethane products may generally be known as “urethanes,” polyurethane is not at all the same as ethyl carbamate (called urethane).
4. These units of urethane have a definite number of atoms of oxygen, nitrogen, carbon, and hydrogen arranged in a particular pattern.

i. Synthesis of urethane (traditional method)

The urethane was synthesis earlier using phosgene, an extremely hazardous chemical

$$\underset{\text{Aniline}}{RNH_2} + \underset{\text{Phosgene}}{COCl_2} \longrightarrow \underset{\text{Isocyanate}}{RNCO} + 2HCl \xrightarrow{R'\text{-}OH} \underset{\text{Urethane}}{RNHCO_2R'}$$

ii. Green synthesis

Mansanto Company has developed a method for the synthesis of urethane eliminating the use of phosgene.

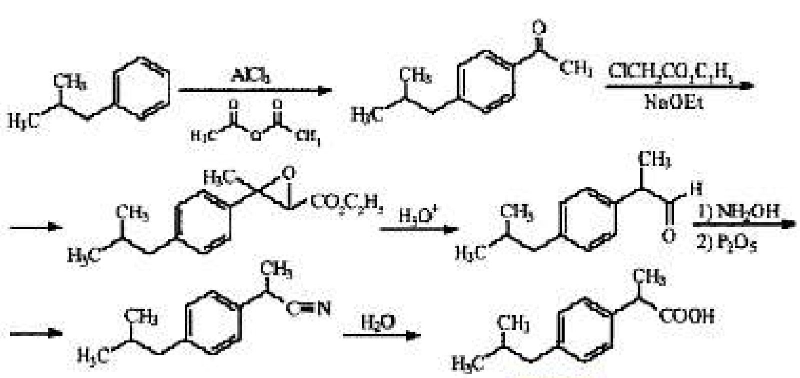
$$\underset{\text{Aniline}}{RNH_2} + \underset{\text{Carbon dioxide}}{CO_2} \longrightarrow \underset{\text{Isocyanate}}{RNCO} + H_2O \xrightarrow{R'\text{-}OH} \underset{\text{Urethane}}{RNHCO_2R'}$$

3. Ibuprofen

Ibuprofen is one of the product used in large quantities for making pharmaceutical drugs like to relieve pain (pain killers) from various conditions such as **headache**, dental pain, menstrual cramps, muscle aches, or arthritis. It is also used to reduce **fever** and to relieve minor aches and pain due to the common cold or flu. Ibuprofen is a nonsteroidal anti-inflammatory drug (NSAID).

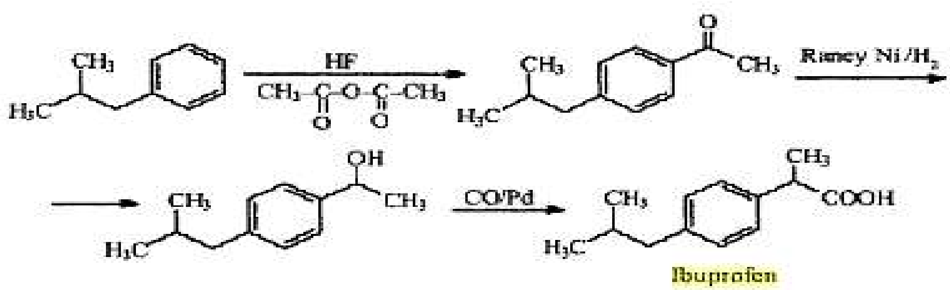
- **The Boots Company PLC** developed and patented the six step brown synthesis of ibuprofen in the 1960s.
- The synthesis process results in millions of pounds of unwanted, unutilized, and unrecycled waste chemical byproducts that have to be treated or disposed of each year.
- The percentage **atom economy** of the brown synthesis of ibuprofen is **40%**→60% (by weight) of all reagent atoms are incorporated into unwanted byproduct or waste.

1. Synthesis of ibuprofen from substituted benzene



Green synthesis of Ibuprofen

- The BHC Companydeveloped and patented a greener, three step synthesis of ibuprofen in 1991.
- Their goal was to develop and put into practice a more efficient and environmentally sensitive method of synthesizing ibuprofen to market.
- The green synthesis provides for a far greater atom economyat **77%** (99% if the acetic acid recovered from the first step is considered).
- This method prevents the formation of millions of pounds of waste and chemical byproduct as well as saves millions of pounds of reactant materials.
  The BHC Company won a Presidential Green Chemistry Challenge Award in 1997 for their development of this synthesis



- There are also other environmental advantages to the green synthesis.
  - The brown synthesis requires auxiliary reagents in stoichiometric amounts. In contrast, the green synthesis is catalytic.
  - The green synthesis uses reagents which are recovered and reused repeatedly (e.g. HF, Raney nickel, and Pd).
  - The green synthesis offers greater throughput which allows larger quantities to be produced in less time resulting in less capital expenditure and significant economic benefits.

Dr. Vaijinath A. Verma, Dept. of Chemistry, S.S. Margol College of Arts, Science and Commerce, Shahabad, Kalaburagi