

GREEN CHEMISTRY: EQUIPPING AND STRENGTHENING CHEMICAL SCIENCES FOR SUSTAINABLE DEVELOPMENT

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OUTLINE OF PRESENTATION

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CHEMISTRY & SOCIETY

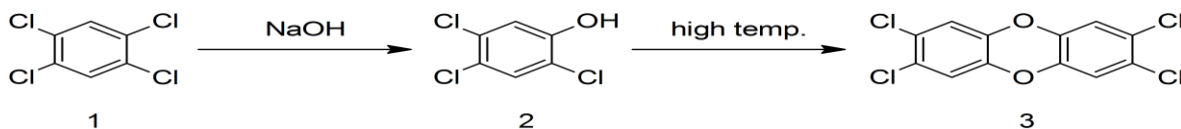
- **Pharmaceutical** –manufacture of drugs (pain killers, antibiotics, heart and hypertensive drugs);
- **Agriculture** –production of fertilizers, pesticides;
- **Food** –manufacture of preservatives, packaging and food wraps, refrigerants;
- **Medical** –disinfectants, vaccines, dental fillings, anaesthetics, contraceptives;
- **Transportation** –production of petrol and diesel, catalytic converters to reduce exhaust emissions;
- **Clothing** –synthetic fibres, dyes, waterproofing materials;
- **Safety** –polycarbonate materials for crash helmets;
- **Sports** –composite materials for rackets, all weather surfaces;
- **Office** –inks, photocopying toners;
- **Homes** –paints, vanishes and polish, detergents, pest killers

CHEMICAL DISASTERS

1956: Minamata disease was first discovered in Minamata city in Japan. It was caused by the release of methylmercury in the industrial wastewater from a chemical factory

1961: Itai-itai disease was caused by cadmium poisoning due to mining in Toyama Prefecture in Japan

1976: The Seveso disaster was an industrial accident that occurred in a small chemical manufacturing plant near Milan in Italy. It resulted in the highest known exposure to 2,3,7,8-tetrachlorodibenzo-p-dioxin in residential population.



1984: The Bhopal disaster was an industrial catastrophe that took place at a pesticide plant owned and operated by Union Carbide (UCIL) in Bhopal India resulting in the exposure of over 500,000 people. It was caused by methyl cyanate (MIC) gas.

1986: The Chernobyl disaster was a nuclear accident at the Chernobyl nuclear plant in Ukraine. It resulted in a severe release of radioactive materials. Most fatalities from the accident were caused by radiation poisoning.

1989: Exxon Valdez, an oil tanker hit a reef and spilled an estimated minimum 10.8 million US gallons (40.9 million litres) of crude oil. This has been recorded as one of the largest spills in United States history and one of the largest ecological disasters.

HISTORY OF GREEN CHEMISTRY

- In **1990** the Pollution Prevention Act was passed in the United States. This act helped create a *modus operandi* for dealing with pollution in an original and innovative way. This paved the way to the green chemistry concept.
- Paul Anastas and John Warner coined the two letter word “green chemistry” and developed the twelve principles of green chemistry.
- In **2005** Ryoji Noyori identified three key developments in green chemistry: use of **supercritical carbon dioxide** as green solvent, **aqueous hydrogen peroxide** for clean oxidations and the use of **hydrogen** in asymmetric synthesis.

CONCEPTS OF GREEN CHEMISTRY

Green Chemistry, or sustainable/environmentally benign chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.

As a chemical philosophy, green chemistry applies to organic chemistry, inorganic chemistry, biochemistry, analytical chemistry and physical chemistry.

- **Minimize:**
 - waste
 - energy use
 - resource use (maximize efficiency)

- **utilize renewable resources**

GLOBAL RECOGNITION OF GREEN CHEMISTRY

- **Australia:** The Royal Australian Chemical Institute (RACI) presents Australia's Green Chemistry Challenge Awards;
- **Canada:** The Canadian Green Chemistry Medal is an annual award given to any individual or group for promotion and development of green chemistry;
- **Italy:** Green Chemistry activities in Italy centre on inter-university consortium known as INCA. In 1999, INCA has given three awards annually to industry for applications of green chemistry;
- **Japan:** In Japan, The Green & Sustainable Chemistry Network (GSCN), formed in 1999, is an organization consisting of representatives from chemical manufacturers and researcher;
- **UK:** In the United Kingdom, the Crystal Faraday Partnership, a non-profit group founded in 2001, awards businesses annually for incorporation of green chemistry;
- **USA:** United States Environmental Protection Agency (EPA);
- **Nobel Prize:** The Nobel Prize Committee recognized the importance of green chemistry in 2005 by awarding Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock the Nobel Prize for Chemistry for "the development of the metathesis method in organic synthesis."

GREEN CHEMISTRY AND SUSTAINABLE DEVELOPMENT

The UN defines sustainable development as ‘meeting the needs of present without compromising the ability of future generation.’

Green chemistry focuses on how to achieve sustainability through science and technology

- To better understand and solve the issue of environmental pollution, many approaches and models have been developed for environmental impact assessments.
- Some of these approaches and models have been successful in predicting impacts for selected chemicals in selected environmental settings.
- These models have joined air and water quality aspects to point and nonpoint sources and have been very useful for the development of emission control and compliance strategies.
- However, some of the approaches and models were aimed primarily at evaluating the quantity of pollutants that could be discharged into the environment with acceptable impact, but failed to focus on pollution prevention.
- The concept of end-of-pipe approaches to waste management decreased, and strategies such as environmentally conscious manufacturing, eco-efficient production, or pollution prevention gained recognition.

THE TWELVE PRINCIPLES OF GREEN CHEMISTRY

Prevention

It is better to prevent waste than to treat or clean up waste after it is formed;

Atom economy

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

Less hazardous chemical syntheses

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

Designing safer chemicals

Chemical products should be designed to preserve efficacy of function while reducing toxicity;

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;

Design for energy efficiency

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

THE TWELVE PRINCIPLES OF GREEN CHEMISTRY(CONT'D)

Use of renewable feedstock

Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure;

Reduce derivatives

A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable;

Catalysis

Reduce derivatives - Unnecessary derivatization (blocking group, protection/ deprotection, temporary modification) should be avoided whenever possible. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents;

Design for degradation

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

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 and

Inherently safer chemistry for accident prevention

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

PROGRESS IN GREEN CHEMISTRY (REAL WORLD CASES)

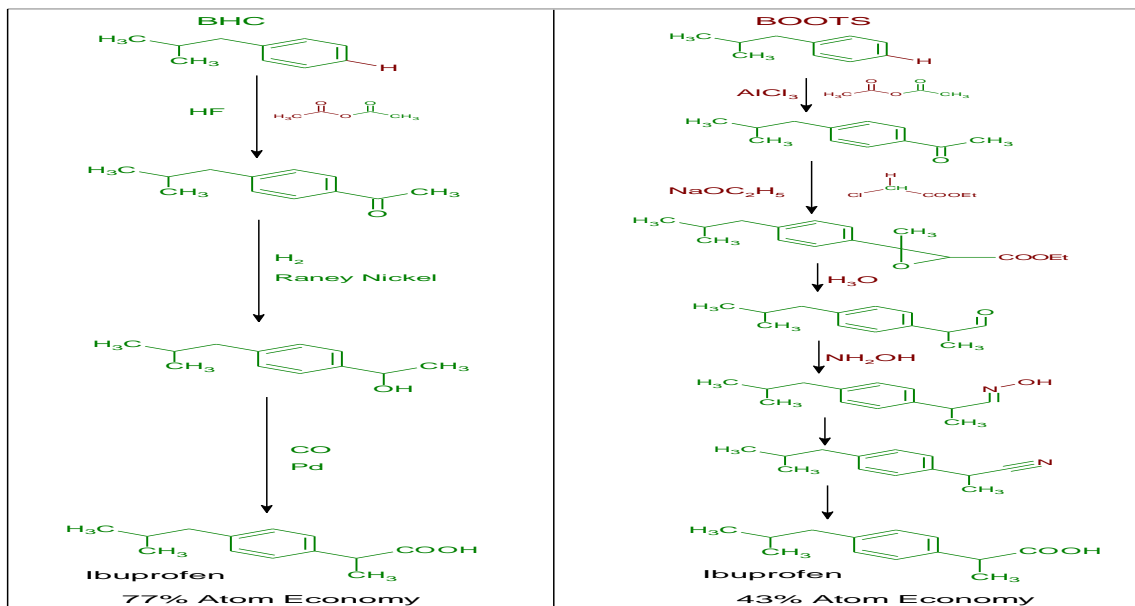
Over the past decade, green chemistry has convincingly demonstrated how fundamental scientific methodologies can be devised and applied to protect human health and the environment in an economically beneficial manner .

Significant progress has been made in key research areas, such as atom economy, alternative synthetic route for feedstocks and starting materials, biocatalysis, green solvent, biosorption, designing safer chemicals, energy and waste management.

ATOM ECONOMY (Synthesis of Ibuprofen)

Atom economy is one of the fundamental principles of green chemistry. Atom economy looks at the number of atoms in the reactants that end up in the final product and by-product or waste.

$$\% \text{ Atom economy} = 100 \times \frac{\text{Relative molecular mass of product}}{\text{Relative molecular mass of reactants}}$$



ALTERNATIVE SYNTHETIC ROUTE FOR FEEDSTOCKS AND STARTING MATERIALS

Production of dimethylcarbonate (DMC) production

DMC is a versatile and environmentally innocuous material for the chemical industry. Owing to its high oxygen content and blending properties, it is used as a component of fuel.

Traditional method for the production of DMC

This method involves the use of phosgene (COCl_2) and methanol (CH_3OH) as shown below:



Alternative route for the production of DMC

This involves the use of copper chloride (CuCl), methanol (CH_3OH), oxygen (O_2) and carbon monoxide.



BIOCATALYSIS

Biobleaching is the extraction of specific metals from their ores through the use of microorganisms such as bacteria. This is much cleaner than the traditional heap leaching using cyanide in the case of gold extraction.

Extraction of gold

This can involve numerous ferrous and sulphur oxidizing bacteria, such as *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* (also referred to as *Thiobacillus*). For example, bacteria catalyse the breakdown of the mineral arsenopyrite (FeAsS) by oxidising the sulphur and metal (in this case arsenic ions) to higher oxidation states whilst reducing dioxygen by H_2 and Fe^{3+} . This allows the soluble products to dissolve.

$$FeAsS(s) \rightarrow Fe^{2+}(aq) + As^{3+}(aq) + S^{6+}(aq)$$

This process occurs at the cell membrane of the bacteria. The electrons pass into the cells and are used in biochemical processes to produce energy for the bacteria to reduce oxygen molecules to water. In stage 2, bacteria oxidise Fe^{2+} to Fe^{3+} (whilst reducing O_2).



They then oxidise the metal to a higher positive oxidation state. With the electrons gained, they reduce Fe^{3+} to Fe^{2+} to continue the cycle. The gold is now separated from the ore and in solution.

GREEN SOLVENT

One of the green solvents is supercritical carbon dioxide (scCO₂). Supercritical carbon dioxide refers to carbon dioxide that is in a fluid state while also being at or above both its critical temperature and pressure (T_c = 31.3 °C, P_c = 1071 psi (72.9 atm) yielding rather uncommon properties. Supercritical carbon dioxide has been used as a processing solvent in polymer applications such as polymer modification, formation of polymer composites, polymer blending, microcellular foaming, particle production, and polymerization.

Reaction of amines with CO₂



BIOSORPTION

Biosorption is one such important phenomenon, which is based on one of the twelve principles of Green Chemistry, i.e., “Use of renewable resources.” It has gathered a great deal of attention in recent years due to a rise in environmental awareness and the consequent severity of legislation regarding the removal of toxic metal ions from wastewaters.

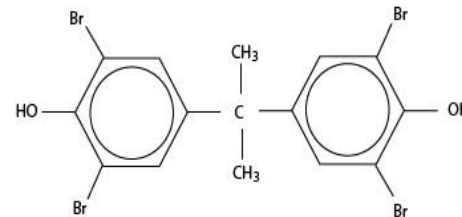
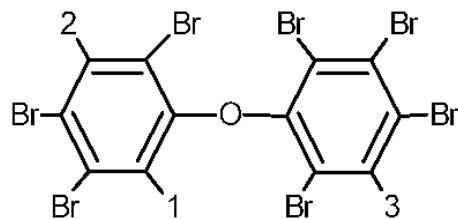
In recent years, a number of agricultural materials such as the following have been used to remove toxic metals from wastewater:

- palm kernel husk,
- modified cellulosic material,
- corn cobs,
- residual lignin,
- wool,
- apple residues,
- olive mill products,
- polymerized orange skin,
- banana husk,
- pine bark,
- sawdust,
- coals,
- **MAIZE TASSEL**

DESIGNING SAFER CHEMICALS

FLAME RETARDANTS

- Flame retardants containing bromine, compared to fluorine, chlorine and iodine have shown to be the most effective and requires a lower loading of materials.
- Brominated flame retardants (BFRs) are structurally diverse group of compounds and BFRs are:
- Polybrominated diphenyl ethers (PBDEs); Tetrabromobisphenol A (TBBPA);



NEW FLAME RETARDANTS

- Decabromodiphenylethane
- tribromophenoxy)ethane
- Pentabromobenzyl acrylate
- Tris(tribromoneopentyl)phosphate

ENERGY

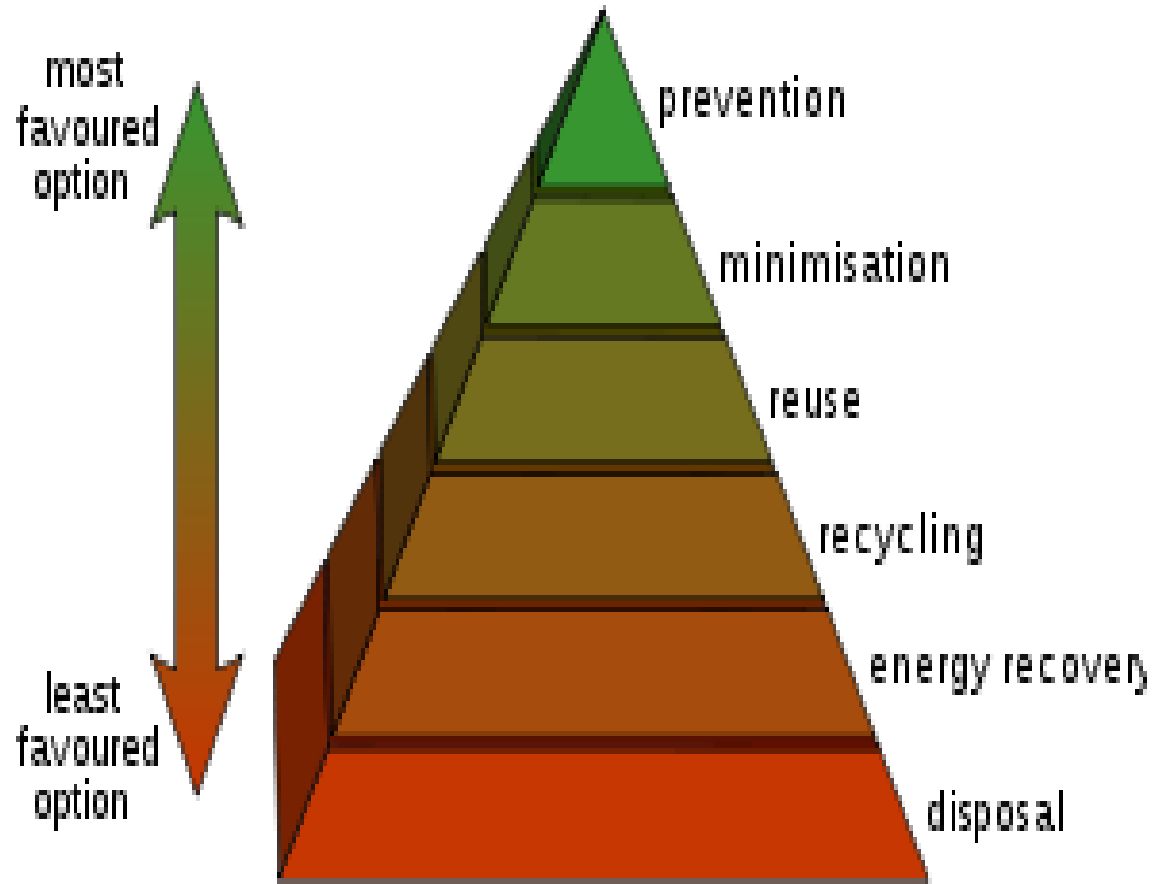
FOSSIL FUEL

- This is dogged with many environmental pollution problems. There is, therefore, a growing need for alternative energy sources to replace fossil fuels. Renewable energy resources that are currently receiving attention include, solar energy, wind energy, hydro energy, fuel cells to mention but four.

SAFER PETROL

- Removal of Pb from petrol;
- addition of ethanol produced from biomaterials to the petrol pool;
- addition of methyl *t*-butyl ether (MTBE) to the petrol pool. MTBE has high octane and
- use of electric vehicles powered by fuel cells.

WASTE MANAGEMENT



CONCLUDING REMARKS

- The challenges in resource and environmental sustainability require more efficient and benign scientific technologies for chemical processes and manufacture of products.
- Green chemistry addresses such challenges by opening a wide and multifaceted research scope thus allowing the invention of novel reactions that can maximize the desired products and minimize the waste and byproducts, as well as the design of new synthetic schemes that are inherently, environmentally, and ecologically benign.
- Therefore, combining the principles of the sustainability concept as broadly promoted by the green chemistry principles with established cost and performance standards will be the continual endeavour for economies for the chemical industry.
- It is, therefore, essential to direct research and development efforts towards a goal that will constitute a powerful tool for fostering sustainable innovation.
- Green chemistry alone cannot solve the pressing environmental concerns and impacts to our modern era, but applying the twelve principles of green chemistry into practice will eventually help to pave the way to a world where the grass is greener.

***CHEERS & THINK
GREEN!***