# Green Chemistry: A Footstep towards Sustainable Development

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ABSTRACT

The word *chemical* comes into our mind with something harmful or negative. This aspect is transmitted from our surroundings - deployed from the maltreatment of chemicals. The concept of “green chemistry” is arisen in response to the need of minimizing the harmful impacts of man-made materials. This branch of Chemical Science is usually described by the 12 principles possessing the key elements: minimizing waste reduction, product toxicity, energy consumption, and enhancing the use of renewable and safer resources. This chapter briefly presents the initiatives taken by the government to improve research in the field of green chemistry; examples and recent advancements in this area as well. The considerations in designing novel-safer chemicals and futuristic trends of greener solvents are also introduced here.

**Keywords – Green chemistry, safer solvents, polluting chemicals, energy efficiency, biodiesel.**

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**Figure 1: The diagrammatic representation of 12 principles of green chemistry**

I. INTRODUCTION

The term “Green Chemistry” corresponds to the design of chemical products and their production processes that reduce or eliminate the production of substances toxic/hazardous to the ecosystem[1–6]. Green chemistry addresses hazards, whether physical (flammability, explosivity), toxicological (carcinogenicity, endocrine disruption), or global (environmental impacts, ozone depletion, climate change) as an inherent property of a molecule. Therefore, the hazard can be addressed through an appropriate design of the structure and the physical/chemical properties associated with it at the molecular level [7]. In other words, green chemistry also refers to the lowering consumption of nonrenewable resources and various approaches for pollution prevention. The concept of green chemistry is evolved in regulatory communities from pollution prevention initiatives. The upgradation made to improve commercial production gave rise to inadvertent harm to our planet and humans. Choked waterways, acid rain, measurable ozone holes, and adverse human and environmental health are some long-term negative effects of these upgrades [8].

The term is similar to sustainable chemistry or circular chemistry [9]. The definition of sustainable chemistry was given by the Organization for Economic Co-operation and Development (OECD) in the 1990s as “a scientific concept that seeks to improve the efficiency with which natural resources are used to meet human needs for chemical products and services” [10]. Sustainable chemistry prioritizes production processes that promote increased product value while intersecting the goals of protecting and enhancing human health and the environment [11]. While environmental chemistry focuses on the consequences of toxic/polluting chemicals on nature.

The amount of hazardous household and industrial wastes can be cut down with the help of the three R principles of the circular economy - reduce, reuse, and recycle with a strong emphasis on “reduce”. Green chemistry still serves a linear economy model (i.e., take-make-use-dispose) and not a circular model that keeps materials in circulation for as long as possible [9].



**Figure 2. Mobius symbol for 3R's principles of circular economy**.

According to the “benign by design” concept, green chemistry bypasses contamination by using environmentally benign processes and designed/innovative products [12].

II. INITIATIVES TO PROMOTE RESEARCH IN GREEN CHEMISTRY

Governments and other organizations have attempted to promote research in green chemistry via the following initiatives and documents:

* Competitive award programs (e.g., the American Chemical Society Award for Affordable Green Chemistry, established in 2007) [13].
* Financing Program of projects and grants, the “Presidential Green Chemistry Challenge” from the US government in 1996[14].
* The scientists and researchers are rewarded for their work in the area of green chemistry. Yves Chauvin (France), Robert Grubbs (USA), and Richard Schrock (USA) shared the 2005 Nobel Prize in chemistry for the development of metathesis [8].
* Many international organizations, such as the Organization for Economic Cooperation and Development (OECD), the International Union of Pure and Applied Chemistry (IUPAC), the European Chemical Industry Council (CEFIC), and the Federation of European Chemical Societies (FECS), adopted green and sustainable chemistry as part of their agenda [15].
* Pollution Prevention Act (1990) EPA. [16, 17]. Pollution prevention (P2) is also known as “source reduction” as presented by the EPA Waste Management Hierarchy. P2 is any practice that prevents pollution at the source level before its creation.
* Paul Anastas- founder of green chemistry, mentioned the 12 principles of green chemistry in his book Green Chemistry: Theory and Practice[3], [18–20]. Now these principles are adopted by the US Environmental Protection Agency.

III. PRINCIPLES OF GREEN CHEMISTRY

Green chemistry encompasses 12 basic principles. These are as follows:

1. Prevent waste: Waste prevention is better than cleaning after formation.
2. Maximize atom economy: Design synthetic methods to maximize the use of whole materials and minimize the byproduct formation.
3. Design less hazardous methodologies: Design synthetic methods that use and generate substances that are less toxic to the environment.
4. Design safer chemicals and effective products: Design chemical products to maintain efficacy and have little or no toxicity.
5. Minimize the use of auxiliary substances: The use of solvents, separating agents and other auxiliary chemicals should be avoided and those used should be safe, whenever possible.
6. Increase energy efficiency: Energy requirements should be minimized for their environmental and economic impact whenever feasible. Chemical reactions should be carried out at room temperature and pressure.
7. Use of renewable starting materials: Whenever technically and economically possible, starting raw materials should be renewable that is usually obtained from agricultural wastes and products.
8. Avoid nonessential derivatization: Derivatization (blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be avoided where possible. Derivatives use extra reagents and create waste.
9. Enhancing catalysis rather than the use of stoichiometric reagents: Make use of selective and reusable catalysts instead of stoichiometric reagents as much as possible. Minimize waste by using catalytic reactions. Catalysts are efficacious in small amounts and can be used many times resulting in waste reduction.
10. Encourage biodegradable chemicals and products: Design chemicals that do not accumulate in the environment after their use and get transformed into harmless degradation products.
11. Evolve analytical methodologies for real-time monitoring: In advance of harmful product formation, analytical methodologies are developed for real-time monitoring and control during syntheses.
12. Lessen the potential for chemical accidents: Design or select the substances- essential for chemical processes, permeating a lower risk of accidents including explosions, fires, and releases to the environment.

Some of the well-known examples of green chemistry are as follows:

1. The metathesis of natural oils and fats is a catalytic reaction that can be started with renewable raw materials like oleochemical feedstocks. Valuable chemical products are obtained with high selectivity under mild conditions either directly or in a few steps [21]. Metathesis of unsaturated fatty ester-methyl *cis*-9-octadecenoate provides a suitable route to unsaturated diesters- dimethyl 9-octadecene-1,18-dioate and internal alkyne- 9-octadecene, in the presence of a suitable catalyst. The reaction given below is an example of a 100% atom-efficient process in which only useful products are obtained and no by-products [19].



**Figure 3: Metathesis of an unsaturated ester of oleic acid.**

1. Adipic acid [HOOC(CH2)4COOH] is used for the production of nylon, lubricants, plasticizers, and polyurethanes. Carcinogenic benzene is used as the standard substrate for the synthesis of this acid. Chemists from the State University of Michigan discovered enzymes in genetically modified bacteria by which glucose-almost inexhaustible, can be converted into adipic acid [22, 23]. Another method of synthesis is- the oxidation of cyclohexene using hydrogen peroxide in the presence of a catalyst. Green chemistry principles - less harmful synthesis, minimal use of organic solvents, better yield, and recyclable compounds, are applicable to this new process [24].



**Figure 4: Schematic representation for the synthesis of adipic acid (a) conventional industrial route and (b) biomass-based green** **route as presented by W. Deng and co-workers.**

1. Biodiesel oil (a mixture of methyl esters and fatty acids) is produced from fats embedded in cultivated plant oils (soya beans) by removing glycerin molecules – a raw material for soap synthesis. Contrary to normal diesel oil, the combustion of biodiesel does not emit harmful sulfur wastes [22, 25].

* Plant oil containing triglyceride + methanol 🡪 biodiesel + glycerin (in presence of KOH)



**Figure 5: Schematic representation for biodiesel synthesis as presented by S. M.Ghoreishi and P. Moein.**

1. Carbon dioxide and water as supercritical fluids (SCFs) are the most frequently used reaction media for fulfilling green chemistry demands. Carbon dioxide as SCF dissolves non-polar compounds and some polar like acetone and methanol. In textile and metal industries, instead of perchloroethylene, liquid carbon dioxide is used for dry cleaning purposes [26, 27]. Trans-critical cycles are thermodynamic cycles in which fluids are used in their supercritical state for heat transport. Compact systems can be framed by the implementation of a single-phase heat transfer method which excludes boiling and the use of higher operating temperatures. CO2 can replace hydrochlorofluorocarbons (HFC) – working fluid in refrigeration systems. Supercritical CO2 promotes the segregation of desired compounds from a mixture followed by easy recovery of itself. Supercritical water is being used as a green solvent for crystalline zinc silicate formation. Ionic liquids – SCF is an excellent bi-phasic system for separation and reactions [28].
2. Room-temperature ionic liquids (RTILs) behave differently from molecular liquids because of their constitution. Low viscosity and no measurable vapor pressure make RTILs environmentally benign reaction media. β glycosylation of glycosyl bromide and organic acids can be achieved through eco-friendly RTILs-enhanced systems [29].
3. Green catalyst: Green catalysts/bio-catalysts are safe alternatives for environmentally unsafe reaction mechanisms [30, 31]. Nano-catalysts[32] are a combination of homogeneous and heterogeneous catalysts [33]. Several pharmaceuticals and chemicals are synthesized from highly toxic nitriles that are xenobiotically derived or naturally occurring, by using nitrilase enzyme[34].



**Figure 6: Correlation between enzymatic catalysis and green chemistry**

IV. RECENT RESEARCH IN GREEN CHEMISTRY

1. Green Ammonia Production: Ammonia plays an important role in the manufacturing of chemical fertilizers. Green ammonia is produced through the green Haber-Bosch process. The hydrogen required for the Haber-Bosch process is generated from water electrolysis - powered by renewable sources, as well as from renewable feedstock via biomass gasification [35]. Biomass gasification is an effective process for the conversion of several types of biomasses into biofuels as syngas (a mixture of CO and H2)[36]. By this method, greenhouse gases emission can be controlled at a very low cost.
2. **Bio-based Polymers**: The bio-based term is concerned with the use of renewable biomass alternatives to unsustainable fossil resources – as raw materials for commodity material and fuel manufacturing. Polyhydroxyalkanoates (PHAs) are bio-based polymers [37] produced by the fermentation of paper mill wastewater, waste polystyrene, and municipal wastewater [38–40].Depending upon structural variations PHAs have various properties and applications. Some physical properties of PHAs make them suitable for single-use products. The PHA produced from the fermentation of biogas from landfills and the air was processed to a thermoplastic named ‘AirCarbon’ by Newlight Technologies [41].
3. **Optimisation of Lactic Acid Production:**Lactic acid has growing applications as its polymers and esters in industries for packaging, pharmaceuticals, and medical because of its biodegradable and biocompatible properties [42]. Agricultural waste from wheat or rice straw, soybean residues, industrial waste from paper and pulp industries, and municipal solid waste can be used as substrates for lactic acid production. The conversion of abundantly available feedstock- starch and lignocellulose materials is tedious and cost-oriented hence genetic engineering is very helpful for economical production processes [43–45].
4. Biodiesel: Bio-diesel is an alternative diesel fuel extracted from renewable resources. The zinc-doped calcium oxide nanocatalyst is a potential and cost-effective agent for the production of sustainable, environmentally friendly, and economic biodiesel from castor oil [46]. Outili *et al.* reported a “maximum biodiesel conversion 100% with a maximum green chemistry balance of 77.36% at catalyst loading (KOH) 2% (w/w), methanol to oil ratio 4:73 at 45 °C.”[47]. The microwave and ultrasonic radiations were applied by Gude *et al*. to produce biodiesel from waste cooking oil with less energy consumption and by-products [48].
5. Plant-mediated synthesis of metal nanoparticles: The metal nanoparticles have found applications in enzyme electrode design, medicine, ecology, analytical methods, and surface-enhanced Raman Spectroscopy (SERS). Plant-mediated synthesis of nanoparticles is an eco-friendly alternative to chemical approaches as it uses plant or plant extracts, is cost-effective, and avoids the use of toxic chemicals [49]. Silver nanoparticles (AgNPs) [50] and gold nanoparticles (AuNPs) are being studied for their antimicrobial and antibacterial properties [51]. There is a growing trend in the synthesis of NPs by applying eco-friendly techniques.

V. DESIGNING SAFER CHEMICALS

Although all the 12 principles are evenhandedly imperative at this juncture, we will highlight the fourth principle i.e. designing safer chemicals and products/Generating effective but non-toxic products.

The fourth principle is indispensable for all of us, as any chemicals we use today have both a present and future impact. The ACS explicates: “Chemical products should be designed to preserve the efficacy of function while reducing toxicity.” [52]. Prior to manufacturing usable items at the industrial level, most of these chemicals were made from daily-life organic ingredients after a few modifications. Complex chemicals were invented to get stronger, more durable products but with complex degradation. This affects the environment and life quality of people who are using and synthesizing these chemicals.

One of the substantial challenges for green chemistry is designing potent chemicals as acknowledged by the American Chemical Society because we still need these modified products in everyday life but their eco-friendly and greener version to make breathing our children a sound environment.

## THE CONCEPT OF DESIGNING SAFER CHEMICALS

As defined in (DeVito and Garret; Designing Safer Chemicals), the concept of designing safer chemicals is:

"The employment of structure-activity relationships (SAR) and molecular manipulation to achieve the optimum relationship between toxicological effects and the efficacy of intended use." [53–56]

The commercial chemicals which are needed to be replaced can be prioritized by using the data available in the United States (U.S.) Environmental Protection Agency’s (EPA’s) Toxics Release Inventory (TRI): the U.S. pollutant release and transfer register (PRTR).

1. STEPS - CONSIDERED IN DESIGNING SAFER CHEMICALS

* **Step 1. Need to know: safe or not?**

Some fundamental questions arise during the initial phase of designing a new chemical. How do we know whether synthesized compounds are safer or not?

Characteristics of the “Ideal Chemical” are [54, 56]

* Because of its good usage potency, less quantity is required to get the job done; hence lesser units need to be manufactured thus in turn less raw material and fewer byproducts.
* Better use efficacy.
* Can be manufactured greenly.
* Has minimal hazards to the ecosystem and global environment as possesses less toxicity, is non-explosive, and is non-flammable [57].
* Readily degrades to environment-friendly products.
* Does not cause biomagnification.
* **“Its Use Does Not Require the Concomitant Use of Other Chemicals that is Toxic.”**
* **Step 2. Procedure/protocol for replacement of compound:**

U.S. EPA classified the chemicals as “existing” which were already in the marketplace in 1976 when TSCA (Toxic Substances Control Act) was enacted and the chemicals that have undergone premanufacture review were listed on TSCA Inventory. EPA classified the substances as “new” which were not on the TSCA Inventory and planned to be used in commerce. The new chemical must be filed with EPA under section 5 of TSCA before starting its manufacturing. The substance is added to the TSCA Inventory as existing if it is found suitable when reviewed by EPA [58].

In European Union (chemicals) are regulated under REACH (*i.e.* Registration, Evaluation, Authorisation, and Restriction of Chemicals) by European Chemicals Agency. REACH identifies biological effects and risks linked to chemicals to improve the protection of human health and the environment.

U.S. EPA’s Toxic Release Inventory (TRI) database helps to know whether a chemical is toxic or not. U.S. Congress passed Emergency Planning and Community Right-to-know Act (EPCRA), Section 313 of which created TRI [59] (EPCRA section 313 Chemical List for Reporting Year 2017 (including toxic chemical categories).

For future research in green design, the probabilistic diagram is a good approach to minimize the chances of being cytotoxic for a newly synthesized chemical. This is an expansion of the molecular design method in which toxicity is measured in a cost-effective rapid manner with minimal use of animals using high-throughput in vitro cytotoxicity assays [60].

* **Step 3. Prepare Hybrid Chemist also named a “toxicological chemist”**

To design safer chemicals, scientists should have integrated knowledge of toxicology, biochemistry, environmental science, and the relationship of pharmacological properties and toxicity with chemical structure. An individual having combined knowledge of all these disciplines is described as a “toxicological chemist” [56, 61]. Considerations in designing safer chemicals can be divided into external – those are external to the organisms and internal – approaches that may get access to these organisms.

VI. FUTURISTIC SCOPE OF DESIGNING SAFER CHEMICALS

Green chemistry encompasses all aspects and types of chemical processes that reduce negative impacts on human health and the environment relative to the current state-of-the-art practices.

1. Mohammed and co-workers [62] studied the substitution of starting material in the polycarbamates (PC) synthesis process. The production of PC was done with ethylene oxide, carbon dioxide, and bisphenol-A instead of phosgene and solvent DCM. The alternative synthetic path with ethylene oxide and carbon dioxide was found safer because

* It replaces both phosgene and DCM.
* By-product is ethylene glycol resulting in less burden of waste treatment [63, 64].



**Figure 6: Schematic representation for synthesis of polycarbamates in a greener way as presented by W. Mohammed and Errayes Asma.**

1. An environment-friendly approach to building molecular complexity, is a one-pot process. Roberta A. Kehoe et al. described a phosphine-free, inorganic base-free, one-pot tandem Mizoroki-Heck olefination, direct arylation, and hydrogenation sequence, to give multicyclic alkylated heteroarenes. A green agenda is motivated to avoid problematic additives and solvents and this avoidance might reduce the bad actors and improve yields in one-pot processes [65].
2. Stable Ionic liquids (ILs)-Lipase Based System can be used as an alternative to biofuel productions and other ester synthesis reactions. ILs increase the potential of reusing the catalyst and lower the risk of adverse environmental impacts. Further research work can be performed to improve the viability of the system[66–68].



1. Safer solvents designed to replace dichloromethane (DCM) for Chromatography Applications: DCM has become a widely used solvent because of its lower boiling point, cost, and ability to solvate heterocyclic compounds but it is carcinogenic and neurotoxic. A. Sharma et al. conducted research on three active pharmaceutical ingredients (API): acetaminophen, aspirin, and ibuprofen. Thin-layer Chromatography, Hansen Solubility Parameter (HSP) theory, and dissolution testing – these approaches were adopted to identify the potential alternative solvents/solvent blends for DCM in pharmaceuticals. The down-selected solvents were further analyzed to find the best-fitting less hazardous substituent. This type of study can be applied to replace solvents [69].
2. A rare example of a three-reaction process was reported by researchers, in which a series of benzochromenes were prepared in good yields. The example shown below demonstrates the power of auto-tandem catalysis; plausible potential for further green chemistry improvement and expansion [65].



**Figure 7: Schematic presentation for synthesis of benzochromene using phosgene (toxic) along with other reagents as presented by R. A. Kehoe and co-workers.**



**Figure 8: Schematic presentation for synthesis of benzochromene without phosgene derivative still gives better yield as presented by R. A. Kehoe and co-workers.**

Part of the text has been dedicated to describing the fourth principle of green chemistry *i.e.* designing safer and greener solvents. Great efforts are still undertaken to promote alternative synthetic pathways.

THE MAJOR CHALLENGE OF GREEN CHEMISTRY IS TO APPLY ITS OWN PRINCIPLES.

VII. CONCLUSION

Green chemistry is used as a sister term for sustainable or circular chemistry. The political involvement helped to launch the Green Chemistry term and implement initiatives to minimize environmental and human health hazards. Recent advancements in the production of eco-friendly chemicals by using renewable resources and alternative pathways can lead to a dazzling future in this field. The chapter focuses on the concept of designing safe and sound chemicals with alternate solvents and catalysts. A little modification in “existing” chemicals and processes may lead to a better or greener one.

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