

Green Chemistry: Intent, Result, and Principles

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ABSTRACT:

Green Chemistry, a concept often misconstrued, goes beyond new technologies and techniques. It is not solely about ionic liquids, microwave chemistry, or biotransformation, but rather about the intent and result of technical application. This review aims to clarify the essence of Green Chemistry, which resides in its principles, not in specific methodologies. We delve into the fundamentals of Green Chemistry, exploring its intent to minimize environmental impact and promote sustainability, and its result, which is the development of environmentally benign products and processes. By examining the 12 principles of Green Chemistry, we provide a comprehensive understanding of this paradigm shift in the field of chemistry. This review serves as a foundation for researchers, chemists, and industries to adopt and implement Green Chemistry practices, ultimately contributing to a more sustainable future.

• KEYWORDS

Green Chemistry, sustainability, environmentally benign, 12 principles, sustainable future.

• INTRODUCTION

Green Chemistry definitions change based upon focus, To answer this elusive question it may in fact be best to first consider what Green Chemistry is not.

Green Chemistry is often described within the context of new technologies. But Green Chemistry is not beholden to ionic liquids, microwave chemistry, supercritical fluids biotransformation, fluoros phase chemistry, or any other new technology. Green chemistry it outside of techniques sewed but rather resides within the intent and the result of technical application.

Some view Green Chemistry as something process. Chemists do already good process chemistry. While often enabling “greener” synthesis, good process chemistry is not equivalent to Green Chemistry. A robust, efficient, and cost- effective chemical process is likely accepted as good process chemistry. The same process examined more rigorously with regard to the twelve principles of Green Chemistry invariably brings to light potential improvements relative to environmental performance. Processes evolve and become “greener” relative to earlier innervations, but only an ideal process embodies Green Chemistry itself. Green Chemistry is not simply good process chemistry, it is the highest efficiency potential that exists for each chemical process, serving as both an inspiration for and a measure of the best process chemistry.

Others feel Green Chemistry is a purely environmental agenda, and a condemnation of industrial chemistry or of scientists. This picture neglects the direct relationship. Between Green Chemistry principles and highly efficient and environmentally benign chemistry, Green Chemistry is a concept for scientists envisioned by scientists for higher efficiency, not a mandate or a condemnation from outside of the scientific community.

In short, Green Chemistry is neither new type of chemistry nor an environmental movement, a condemnation of industry, new technology, or “what we do already”, Green Chemistry is simply a new environmental priority when accomplishing the science already being performed regard less of the scientific discipline or the techniques applied. Green Chemistry is a concept driven by efficiency coupled to environmental responsibility.

Green Chemistry insists that our synthetic objectives are achieved while assuming additional considerations related to the unnecessary environmental burden created during operations. If using a toxic reagent, one should inquire if a less toxic reagent might accomplish similar ends. A literature search may provide no current alternative with similar efficiency and reduced toxicity, but many do not realize that the simple act of inquiry toward reduced toxicity already indicates a new priority and intent, a higher level of awareness and environmental stewardship, and is Green Chemistry! In some cases a safer reagent will exist. Application will improve the process environmental profile and reduce risk related to working with a toxic reagent while maintaining or improving synthetic efficiency. Some believe environmental priority will add time and cost. Just the opposite, time and cost are reduced by incorporating higher synthetic efficiency the first time, and new methods can be applied toward parallel and future endeavors to enhance overall productivity.

Pharmaceutical Green Chemistry begins with medicinal (discovery) chemistry. The prevalent argument against this asserts that process. Routine process R&D can deliver significant improvement relative to economy and the environment and is frequently characterized as Green Chemistry; but it is important to understand that good process chemistry and Green Chemistry are not interchangeable terms (vide supra). Pharmaceutical Green Chemistry is the ideal that one strives for, and the pursuit of this ideal will lead to ever better process chemistry.

All scientists, regardless of their role, should embrace Green Chemistry principles to impact all facets of pharmaceutical science throughout the life of a pharmaceutical product.

- **HISTORY**

Green chemistry was first used in 1991 by P. T. Anastas in a special program launched by the US Environmental Protection Agency (EPA) to implement sustainable development in chemistry and chemical technology by industry, academia and government. In 1995 the annual US Presidential Green Chemistry Challenge announced. Similar awards were soon established in European countries. In 1996 the Working Party on Green Chemistry was created, acting within the framework of International Union of Applied and Pure Chemistry. One year later, the Green Chemistry Institute (GCI) was formed with chapters in 20 countries to facilitate contact between governmental agencies and industrial corporations with universities and research institutes to design and implement new techniques. The first conference highlighting green chemistry was held in Washington in 1997, since that time other similar scientific conferences have soon held on a regular basis. The first books and journals on and journals the subject of green chemistry were introduced in the 1990s, including the Journal of Clean Processes and Products (Springer-Verlag) and Green Chemistry, sponsored by the Royal Society of Chemistry. Other journals, such as Environmental Science and Technology and the Journal of Chemical Education, have devoted sections to green chemistry. The actual information also may be found on the Internet.

- **IDES OF GREEN CHEMISTRY**

The concept of green chemistry has appeared in the United States as a common research program resulting from interdisciplinary cooperation of university teams, independent research groups, industry, scientific societies and governmental agencies, which each have their own. Programs devoted to decreasing pollution. Green chemistry incorporates approach to the synthesis, processing and application of chemical substances in such a manner as to reduce threats to health and the environment. This new approach is also known as

- Environmentally benign chemistry
- Clean chemistry
- Atom economy
- Benign-by-design chemistry

Green chemistry is commonly presented as a set of Twelve principles proposed by Anastas and Warner. The principles comprise instructions for professional implement new chemical compounds, new chemists to syntheses and new technological processes. The first principle describes the basic idea of green chemistry protecting the environment from pollution. The remaining principles are fecund on such issues an atom economy, toxicity, solvent and other media using consumption of energy, application of s raw materials from renewable sources and degradation of chemical products to simple, nontoxic substances that are friendly for the environment.

- **12 PRINCIPALS 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 he 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 une and generate substances that possess lit- tle 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 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.

7.Use of Renewable Feed stocks-

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/deportation, 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.

The selected examples for implementing the 12 principles in laboratory and industry are presented in table 1.

Table 1. Examples of implementation of green chemistry principles into practise.

Nr	Principle	Examples:
1	Prevention	Use of solvent-less sample preparation techniques [2]
2	Atom Economy	Hydrogenation of carboxylic acid to aldehydes using solid catalysts
3	Less Hazardous Chemical Syntheses	Adipic acid synthesis by oxidation of cyclohexene using hydrogen peroxide [3]
4	Designing Safer Chemicals	New, less hazardous pesticide (e.g. Spinosad) [4]
5	Safer Solvents and Auxiliaries	Supercritical fluid extraction, synthesis in ionic liquids [5]
6	Design for Energy Efficiency	Polyolefins – polymer alternative to PWC (polymerization may be carried with lower energy consumption) [6]
7	Use of Renewable Feedstocks	Production of surfactants [7]
8	Reduce Derivatives	On-fiber derivatization vs derivatization in solution in sample preparation [8]
9	Catalysis	Efficient Au(III)-catalyzed synthesis of β -enamiones from 1,3-dicarbonyl compds. and amines [9]
10	Design for Degradation	Synthesis of biodegradable polymers [10]
11	Real-time analysis for Pollution Prevention	Use of in-line analyzers for wastewater monitoring
12	Inherently Safer Chemistry for Accident Prevention	Di-Me carbonate (DMC) is an environmentally friendly substitute for di-Me sulfate and Me halides in methylation reactions [11].

- **SCIENTIFIC CHALLENGE**

Meeting the criteria of providing payback within a short time frame presents a major scientific challenge. Broadly, green chemical process research can be divided into three categories: alternative feedstocks, alternative solvents, and alternative synthetic pathways, many of which involve novel catalysis.

Alternative feedstocks. One proven approach, already widely implemented industry, is to use the waste from one process as a feedstock or reagent in next. A potential difficulty is that if the production of many quite disparate products becomes linked, leading to problems if demand for one of them changes dramatically. A more radical approach is to move from hazardous, resource-depleting materials such as petroleum to those from renewable or biologically derived sources. For example, bio-derived lactic acid is now being used as a feedstock for large scale industrial polymer production. Renewable feedstocks are often highly amenable to bioprocessing by enzymes, but represent a chemical challenge: Biomolecules such as sugars oxygenated than petrochemical hydrocarbons, and may therefore require changing the chemistry from oxidation to reduction to manufacture a particular end-product.

The simplest alternative feedstock is CO₂. Making chemicals from CO₂ would not only conserve petroleum but also reduce CO₂ emissions. However, CO₂ is thermodynamically extremely stable and therefore difficult to activate chemically. Nevertheless, progress has been made in incorporating CO₂ into polymers, and in reacting it with H₂ to make formic acid, HCO₂H. The key is the design of new catalysts, and techniques such as immobilization or ultrafiltration, for separating high-value catalysts from the products so that they can be recycled.

Alternative solvents. Organic solvents are a major source of waste, and their efficient control can produce a substantial improvement in the environmental impact of a process. The most elegant way to avoid problems with solvents is not to use them, an approach that has been widely exploited in the paints and coatings industries. Recently, Raston et al. described organic reactions that can be carried out merely by grinding the reagents together with a catalyst, a process that is both cleaner and quicker than the conventional reactions. The experiment may not be easy to scale up to an industrial level but it has nevertheless caused a paradigm shift in synthesis of a whole class of compounds that were previously tedious or difficult to make.

Fig. Part of the multipurpose plant at Consett, Co Durham, United Kingdom, for chemical manufacture in supercritical CO₂. The plant is a good example of a green technology, developed in a university, being evaluated on a commercial scale in industry. More such trials are needed to implement new green chemical technologies. [Photo courtesy of Thomas Swan & Co. Ltd.]



Most reactions do, however, require a solvent, and a green chemical process must necessarily involve an environmentally acceptable solvent. Much current research focuses on two classes of alternative solvents: supercritical fluids and ionic liquids. Supercritical fluids are gases that are nearly as dense as liquids, while ionic liquids are salts of highly asymmetrical ions with melting points below or close to room temperature. The cheapest supercritical fluid, CO₂, has solvent

properties similar to those of light hydrocarbons, apart from an unusually high affinity for fluorocarbons. Its properties can be “tuned” by changing the applied pressure, leading to unusual chemical effects not easily achieved in more conventional solvents. Applications include dry cleaning. Ionic liquids are chemically diverse owing to the huge number of possible cation/anion combinations that can be synthesized. A very broad range of chemical reactions from alkylation and polymerization to biocatalysis and electroplating have already been carried out in these solvents, although as yet none has been carried out on an industrial scale.

Alternative synthetic pathways. Most new pathways that lead to cleaner chemistry involve catalysts. A century ago, catalysts were not widely used in the chemical industry. Today, no petrochemical company and few chemical companies would be competitive without their use. The design of selective catalysts is crucial the future of green chemistry

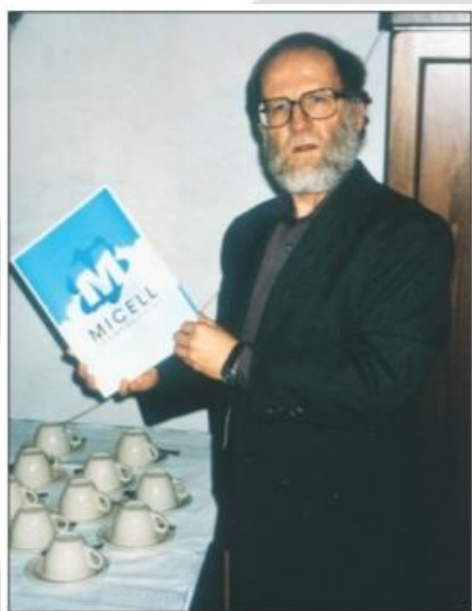


Fig. The late Joe Breen, founding director of the US Green Chemistry Institute (18), wearing one of the first suits dry-cleaned in CO₂. [Photos: M. Poliakoff]

because improved catalysis can reduce the number of stages in a given process and hence reduce its environmental impact. For example, a novel catalytic step has almost halved the number of stages needed to manufacture the analgesic ibuprofen and has also eliminated the toxic solvent solvent CCl₄ from the process. Similarly, Pfizer has introduced a new process, designed on green chemistry principles, that greatly reduces waste in manufacturing sertraline, the active ingredient in the anti depressive drug Zoloft.

The design of safer chemicals will necessarily change the detailed synthesis that is needed for a particular product. Nevertheless, there is still a major need for concerted re- search to improve the selectivity and performance of catalysts, Spent catalysts left at the end of a reaction also contribute to chemical waste, particularly because many contain toxic heavy metals. Research into catalyst reuse and recycling is still in its infancy. These factors should favor the use of enzymes biocatalysts, which are often highly selective and do not involve toxic metals. Despite many commercially successful biocatalytic processes (such as the manufacture of the sweetener aspartame), much research remains to be done before biocatalysts can be used routinely throughout the chemical industry.

- **GREEN SAMPLE PREPARATION METHODOLOGIES FOR FOOD SAMPLE**

Analytes in foods are distributed randomly, making them complex heterogeneous matrices. Therefore, analyzing food requires sampling, homogenization, and sample preparation to increase precision and accuracy. Typically, samples are prepared by storing, homogenizing, diluting, filtering, extracting, and cleaning. An effective sample preparation protocol eliminates matrix interference and preconcentrates analytes, thus improving sensitivity, selectivity, and overall performance.

Recently, analytical scientists and practitioners either developed new methodologies or upgraded the traditional extraction methods to fulfill the principles of green chemistry. In the most general sense, pretreatment methods can be considered as two steps: an extraction and clean-up method and an extraction and preconcentration method. Even so, some techniques can simultaneously remove interfering substances and extract the target analytes. In addition, integration of extraction and preconcentration into a single process is also possible. Hence, existing green sample preparation methods were categorized into three major groups according to their characteristics, which mainly include liquid-based extraction, sorbent-based extraction, and gas-based extraction.

1. Liquid-based extraction techniques

Liquid-liquid extraction (LLE) is one of the most used sample preparation techniques in food analysis. LLE involves extracting analytes from an aqueous sample into a water-immiscible solvent according to their relative solubility. LLE has many shortcomings, such as long preparation times, solvent requirements, analyte loss, sample contamination, and low sensitivity. Liquid-phase microextraction (LPME) is an LLE-based microextraction technique that has been developed to overcome LLE's disadvantages and implies green chemistry principles. Herein, LPME relies on using a minimal amount of organic solvent (microliter) to achieve the isolation and preconcentration of the analytes. Moreover, the extraction takes place between the aqueous sample phase (donor phase) and a water-immiscible solvent extraction phase (acceptor phase). Even though LPME uses organic solvents, it is considered a green extraction technique since less than 100 μL of solvent is used. LPME can be divided into the following sections:

- Single-Drop microextraction (SDME)
- Hollow-Fiber liquid-phase microextraction (HF-LPME)
- Electro-membrane microextraction (EME)
- Dispersive liquid-liquid microextraction (DLLME)
- QuEChERS
- Ultrasound-Assisted back extraction (UABE)
- Ultrasound-Assisted extraction (UAE)
- Microwave-Assisted extraction (MAE)
- Pressurized liquid extraction (PLE)
- Supercritical fluid extraction (SFE)
- Enzyme-Assisted extraction (EAE)

2. Solid-based extraction techniques

The solid-based extraction technique is widely used for liquid or solid samples dissolved or extracted into liquid form [12,13]. The method can also be applied to specific gaseous samples by trapping them on sorbents or derivatizing them in situ with reactive chemicals [125]. Herein, we categorized them into the following groups:

- Solid-Phase microextraction (SPME)
- Dispersive solid-phase extraction (DSPE)
- Microextraction in packed sorbent (MEPS)
- Stir-Bar sorbent extraction (SBSE)
- Fabric phase sorptive extraction (FPSE)

3. Gas-based extraction techniques

Headspace (HS)

As a sample preparation method, HS extraction has proven useful for a wide range of VOCs in the headspace, reducing matrix interferences for food substrates. HS extraction relies primarily on the adsorption of analytes on fiber coatings. HS extraction can be operated in four modes, static HS (S-HS), dynamic HS (D-HS), purge-and-trap (P&T-HS), and full evaporation–D-HS system (FED-HS).

4. New green solvents

In recent years, alternative solvents have gained popularity for sample preparation because they can replace highly toxic, volatile, flammable organic solvents.

Ionic liquids (ILs) are an attractive alternative to traditional organic extraction solvents for ionic liquid DLLME (IL-DLLME). In addition, their tunable physicochemical properties make them a desirable choice for this application.

ILs are organic salts that contain organic cations such as imidazolium, pyridinium, and pyrrolidinium, as well as inorganic anions like chloride and dicyanamide. They have a melting point lower than 100 °C. As green solvents, they are known for their unique properties, like negligible vapor pressure at a wide range of temperatures, high thermal stability, and high viscosity. Despite this, their use for sample preparation techniques was originally restricted due to their density and viscosity, a situation that was remedied by tuning their constituent ions .

Deep eutectic solvents (DESs) are a new generation of solvents synthesized by combining hydrogen bonding acceptors (HBAs) and hydrogen bonding donors (HBDs) to form eutectic mixtures via hydrogen bonds that melt at a lower temperature than its pure constituents .

Natural DESs (NADESs) have been synthesized with various natural molecules, including choline chloride, organic acids, sugars, and amino acids, along with water as a third component.

As with ILs, DESs and NADESs have properties such as tunable solubility in organic solvents, low vapor pressures, high conductivity, and thermal stability. While they are less toxic than ILs, they are also more biodegradable. Furthermore, their synthesis is inexpensive, less complex, and does not require organic solvents, thereby reducing their environmental impact. On the other hand, most organisms can metabolize NADES, which makes them highly biocompatible. They can also be reused and recycled.

DESs have replaced all the organic solvents in the extraction techniques above. For example, dispersive Liquid-Liquid microextraction, solid-phase microextraction , headspace single-drop microextraction, and direct immersion single-drop microextraction .

- **ADVANTAGES OF GREEN CHEMISTRY**

1. Does not release anything detrimental into atmosphere
2. Bring economic profits to certain areas
3. Need less maintenance
4. It is renewable which means will never run out
5. Slow the impacts of global warming by reducing CO2 emissions

- **DISADVANTAGES OF GREEN CHEMISTRY**

The basic task of green chemistry is designing chemical products and processes that reduce or eliminate harmful substances. This goal is also the biggest of green chemistry that is reflected in time, costs and lack of information. In specific, converting from an old, traditional product to a new “green” product, Design of a new product and process

is often not easy and quite expensive, no known alternative chemical or raw material inputs, also there is a lack of unity on what is considered safe. With the high cost of implementation and the lack of information, that will lead to a lack of green chemistry where is no identified alternative in order to used chemical raw materials or alternative technologies for green processes. Moreover, there is also a lack of human skills. Ionic liquids are the future of green chemistry. Although there is no doubt that those are valuable in chemical synthesis. When applying 12 principles that define green chemicals, ionic liquids do not look principally green. While, as is well known, ionic liquids are slightly volatile due to the low vapor pressure, yet it is only one of the several things that make a substance green. For instance, ion-based, fluoro-anion-based and Imidazole-based liquids are expected to be poisonous but cannot reach the environment through evaporation. The problem is that most ionic liquids are water-soluble and can simply reach the biosphere via that pathway.

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